

932
4768

ARS 72-51
September 1966

**PROCEEDINGS,
OF THE
CITRUS
CHEMISTRY AND UTILIZATION
CONFERENCE**

U. S. DEPT. OF AGRICULTURE
NATIONAL AGRICULTURAL LIBRARY

NOV 2 - 1966

CURRENT SERIAL RECORDS

Held at
Winter Haven, Fla.
October 13, 1965

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

FOREWORD

The Citrus Processing Conference is sponsored annually by the Southern Utilization Research and Development Division to present the results of recent studies in citrus chemistry and processing, and to provide for an exchange of information that will benefit future research.

This Conference was held October 13, 1965, at the Landmark Motor Lodge in Winter Haven, Florida, with L. G. MacDowell, Florida Citrus Commission, Lakeland, Florida, serving as General Chairman. The program was developed by B. H. Wojcik, Assistant Director, under the guidance of C. H. Fisher, Director, in cooperation with staff members, and advisers representing the citrus industry.

These proceedings report or summarize the statements of the various speakers during the conference and gives an account of the discussions which followed. If further details are desired regarding any subject presented here, they may be obtained by communicating with the author concerned.

Underscored numbers in parentheses refer to references or literature cited at the end of the article. The figures, references, and tables are reproduced essentially as they were supplied by the writer of each paper.

Mention of companies or products used in this publication are solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

TABLE OF CONTENTS

	Page
L. G. MacDowell, General Chairman	
Session I	
David W. Hamrick, Chairman	
Alcohols in Some Citrus Oils (Summary)	
G. L. K. Hunter and M. G. Moshonas (Presented by M. G. Moshonas)	1
Rapid Estimation of Volatile Oil in Citrus Juices by Bromate Titration (Summary)	
W. C. Scott and M. K. Veldhuis (Presented by W. C. Scott)	2
Contribution of Orange Oil Components to Aroma (Summary)	
W. L. Stanley, K. L. Stevens, R. A. Flath, and D. G. Gaudagni (Presented by W. L. Stanley)	3
Progress in Bitterness Studies on Orange Peel (Summary)	
L. J. Swift	4
Investigation of the Paraffin Waxes in Cold-Pressed Orange Oil (Summary)	
G. L. K. Hunter and W. B. Brogden, Jr. (Presented by M. K. Veldhuis)	5
Significance of Recent Research on Grapefruit Flavonoids	
R. F. Albach	6
Session II	
R. W. Kilburn, Chairman	
New Grapefruit Constituents and Their Importance (Summary)	
E. A. Beavens, V. P. Maier, and W. D. MacLeod (Presented by E. A. Beavens)	10
A Review of Procedures for Production of Grapefruit Crystals Using the Crater-Type Foam-Mat Dryer (Summary)	
R. E. Berry, O. W. Bissett, and C. J. Wagner, Jr. (Presented by R. E. Berry)	12
Dehydration of Citrus Juices	
J. H. Nair	13
Attendance List	23
List of Citrus Publications and Patents (September 1, 1963 - August 31, 1965)	27

PROCEEDINGS OF THE CITRUS CHEMISTRY AND UTILIZATION CONFERENCE

HELD AT WINTER HAVEN, FLA., OCTOBER 13, 1965

L. G. MacDowell, General Chairman

Dr. Mac Dowell, General Chairman, called the conference to order and introduced Dr.

F. R. Senti who welcomed those in attendance on behalf of the Agricultural Research Service.

SESSION I

David W. Hamrick, Chairman

ALCOHOLS IN SOME CITRUS OILS

(SUMMARY)

by
G. L. K. Hunter and M. G. Moshonas
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by M. G. Moshonas)

The use of citrus oils by the food industry to bestow a share of the characteristic flavor to many products makes it essential that the constituents of each oil be positively identified so that their contribution to flavor can be determined. Identification of the constituents can be utilized further in determining the changes which occur during maturation, processing and storage. The arrival of more refined analytical tools and techniques is extending efforts toward the identification of the constituents of citrus oils.

The alcoholic composition of citrus oils, other than orange, has received very little attention. This investigation includes a procedure for isolation of the alcohols from Florida cold-pressed oils of grapefruit, lemon, lime, and tangerine using a nonaqueous extraction procedure. The method utilizes the partitioning of the oil between glycerol and the hydrocarbons of the oil itself. Accordingly, 1 liter of the citrus oil and 500 ml. of glycerol were vigorously shaken in a 2 liter separatory funnel for 20 minutes. The lower (glycerol) layer was removed and extracted with four 125 ml. portions of ethyl ether. The combined ether extracts were washed with

100 ml. of water. The ether was then removed under reduced pressure to yield an alcohol-rich residue. This residue was further enriched by column chromatography, using neutral alumina as the adsorbent. The alcohols in each were separated by gas chromatography and the materials represented by each peak were collected and analyzed by infrared and mass spectroscopy.

Twenty alcohols were identified from grapefruit oil. They were cis-, and trans-linalool oxide, linalool, octanol, cis-, and trans-2,8-p-menthadiene-1-ol, nonanol, α -terpineol, decanol, citronellol, nerol, geraniol, cis-, and trans-carveol, dodecanol, 1,8-p-menthadiene-9-ol, nerolidol, elemol, 8-p-menthene-1,2-diol, and o-phenyl phenol. o-Phenyl phenol is used by the citrus industry as a fungicide.

The 9 alcohols found in lemon oil were: linolool, octanol, terpinene-4-ol, nonanol, α -terpineol, decanol, nerol, geraniol, and 1,8-p-menthadiene-9-ol. The alcohols found in lime oil were: linolool, octanol, terpinene-4-ol, nonanol, α -terpineol, decanol, nerol, and geraniol.

1/ Present Address: The Minute Maid Company, Orlando, Fla.

Seventeen alcohols which were identified from tangerine oil were: linalool, octanol, cis-, and trans-2,8-p-menthadiene-1-ol, nonanol, α -terpineol, citronellol, nerol, geraniol, trans-carveol, 1,p-menthene-9-ol, dodecanol, 1,8-p-menthadiene-9-ol, elemol, thymol, 8-p-menthene-1,2-diol, and o-phenyl phenol.

DISCUSSION

Question: What portion of the citrus oil does the alcohol fraction comprise?

M. G. Moshonas: We were primarily interested in the identification of the alcohols in the various citrus oils and did not make a

detailed study on the quantity. However, from the figures I do have I would say about 0.5 percent.

Question: In any of your chromatographic work, were any of the compounds as characteristic of orange as nootkatone was of grapefruit?

M. G. Moshonas: No. It appears the characteristic odor comes from a complex mixture of compounds. However, all the work on the isolation and identification of constituents of orange oil has not been completed and compounds may be eventually isolated which are characteristic of orange.

RAPID ESTIMATION OF VOLATILE OIL IN CITRUS JUICES BY BROMATE TITRATION

(SUMMARY)

by

W. C. Scott and M. K. Veldhuis
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by W. C. Scott)

Some oil from the peel of citrus fruit is necessary in juice products to provide optimum flavor, but too much is objectionable and upper limits are set by regulations. Processors, therefore, need to control the amount present in their finished products. Measurements of oil recoverable by distillation has been accepted as a satisfactory approximation, as peel oil contains 90-95 percent d-limonene which is readily steam-distillable and immiscible with aqueous condensate. The 1.5 hours required to distill enough oil for measurement by volume (official Clevenger method) is a serious problem in the high volume, fast operating citrus juice processing industry. Attempts to shorten the time required for oil determinations have included microvolumetric methods, or the correlation of oil content with turbidity formed by distilling the oil with miscible solvent, then diluting with water. These methods have not been entirely satisfactory.

The novelty of the method proposed here lies in the bromination of d-limonene distilled

with miscible solvent. The method consists of adding 25 ml. 2-propanol to 25 ml. juice and distilling over about 30 ml.; acidifying the distillate with 10 ml. HCl (1+2); and titrating with 0.025 N potassium bromate-bromide solution. In acid solution the bromate releases bromine which combines with d-limonene at each of its two double bonds. When all the d-limonene is used up, the first excess of bromine completely decolorizes methyl orange used as an internal indicator. One ml. reagent is equivalent to 0.001 ml. d-limonene, or 0.004 percent by volume of a 25 ml. sample.

Recovery of d-limonene added to citrus juices in concentrations from 0 to 0.052 percent was 100+1 percent, indicating a high degree of accuracy. Replicate determinations on model systems and on orange, grapefruit and tangerine juices seldom varied more than 0.001 percent oil, indicating excellent precision. Recoveries were slightly higher than by the Clevenger method.

Time required for distillation is about 3 minutes, and less than 7 minutes for the complete determination. The procedure is

simple, and the cost of equipment and supplies is low.

CONTRIBUTION OF ORANGE OIL COMPONENTS TO AROMA

(SUMMARY)

by

W. L. Stanley, K. L. Stevens, R. A. Flath, and D. G. Guadagni
Western Utilization Research and Development Division Fruit Laboratory
Albany, Calif.

(Presented by W. L. Stanley)

A new sesquiterpene aldehyde (β -sinensal) has been isolated from cold-pressed orange oil. The structure has been elucidated. Its relation to α -sinensal^{1/} both in structure and in percentage of the whole oil is to be presented. The odor threshold of α -sinensal has been determined and is lower than that of vanillin. It is in the range of some sulfur compounds. The low threshold and relatively high percentage (~ 0.1 percent) of α -sinensal in cold-pressed peel oil make it one of the major components of oil aroma.

The relationship between sensory responses and objective measurements has been a problem confronting those involved in flavor and aroma research. A technique has been developed in which gas chromatography and sensory procedures (sniffing at column outlet) are combined to show which components contribute to the aroma of a fruit. Red Delicious apple essence was injected into a gas chromatograph, and the emerging components sniffed by panel members. These data permit conclusions concerning the relative importance of each peak.

DISCUSSION

Question: Concerning odor peaks 1 through 8, if they were mixed with peak 9 or No. 9 up would you get a better carrying or lower threshold?

W. L. Stanley: The panel could not tell them apart on a triangle test.

Question: Was there any difference in peaks 9 through 13 in response?

W. L. Stanley: Eleven was the one with strongest apple aroma. The others had apple flavor character also but of a different type.

Question: What is the identity of 11?

W. L. Stanley: We don't know yet, but we know that normal hexenal is one of the important components. Some Germans have already reported this.

Question: Have you separated these three apple-flavored peaks to be certain that the "apple" in each large peak isn't due to tailing from the small, intensely apple peak? Have you been able to find anything on these chromatographs that permits you to distinguish between the essence from Delicious and Jonathan varieties?

W. L. Stanley: We haven't done that yet. This is what we are going after - to try to get down inside of this and find out with Jonathan, Delicious, and others what are the compounds characteristic of each of these, but we do not know now. There is some chance of contamination of adjacent peaks but recent work with more efficient equipment has demonstrated that there are several well separated peaks with apple aroma of varying character.

Question: What about the identification of peaks 9 through 13?

W. L. Stanley: Not yet-we are working on them.

^{1/} Stevens, K. L. Lundin, R. E., and Teranishi, R. J. Org. Chem. 30, 1960 (1955).

Question: One other question. Would this be a good way of checking the fold of apple essence?

W. L. Stanley: I think so, yes it could be used. The dilution determination, of course, is what tells you this, if you are diluting the right peak. You have to select from the whole oil that part that is important.

Question: For the same fold in apple essence, do you find any major variations with peaks 9 to 13 between grades and between varieties?

W. L. Stanley: I don't know yet. We haven't done this but we certainly intend to.

PROGRESS IN BITTERNESS STUDIES ON ORANGE PEEL

(SUMMARY)

by

L. J. Swift

Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

Data were presented on the bitterness and yield of juice pressed from orange peel collected over the 1962-63 and 1963-64 seasons. Yields ranged from 13.5 to 47.6 percent with soluble solids ranging from 11.2 to 16.4 percent. Bitterness was expressed as the minimum percentage of the juice that could be detected when added to orange juice and the range found was 3 to 8 percent.

Benzene extractables on the juices mentioned above varied between 312 and 956 mg. per liter of juice. The extractable substances were separated into phenolic, neutral, and lactone fractions which were found in the following ranges:

Phenolic	18.8-51.2
Neutral	42.6-71.8
Lactone	0.0-17.3

No particular correlation was apparent either in the amounts of extractables or fractions thereof with the bitterness of the peel juices, but since the neutral fractions were generally the largest and were bitter, further work was concerned with these. The threshold values, expressed as parts per million, added to orange juice ranged between 18 and 44 with most of the values falling between 27 and 32.

Taste contributions of the neutral fraction to the bitterness of peel juices were calculated and found to range between 35 and 76 percent.

Seven of the above neutral fractions were analyzed for methoxylated flavones by a method developed recently by the author. The ranges of the percentages found are given below:

Tangeretin	2.1-14.8
Tetra-O-methylscutellarein	6.1-10.3
3, 5, 6, 7, 8, 3', 4' -Heptamethoxyflavone	7.6-11.0
Nobiletin	20.6-30.6
Sinensetin	18.7-28.2

On the basis of these 5 flavones, it was possible to account for from 57.8 to 84.6 percent of the neutral fractions.

Using a method developed by Chandler in Australia, it was shown that a sample of bitter Florida orange concentrate contained limonin in an amount that Chandler classifies as strongly bitter. This is the first time this substance has been reported in the edible portions of Florida citrus although it has long been known to be a constituent of the seeds.

INVESTIGATION OF THE PARAFFIN WAXES IN COLD-PRESSED ORANGE OIL

(SUMMARY)

by

G. L. K. Hunter and W. B. Brogden, Jr.^{1/}
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by M. K. Veldhuis)

This study is a part of a comprehensive program on the chemical composition of cold-pressed orange oil. In this case the higher boiling hydrocarbons or paraffin waxes were studied. Mass spectrometry was used extensively in the identification of these compounds.

The paraffins were first concentrated by fractional distillation under vacuum and separated by column chromatography. Oxygen containing compounds were separated on a column of basic alumina with n-hexane as the eluting agent. Individual paraffins were separated on a 1/4 in. by 6.5 ft. column containing 10 percent Carbowax 30M on acid-washed firebrick. As each peak emerged from the gas chromatograph it was trapped in a glass capillary. The

material was transferred from the capillary to the Bendix "Time-of-Flight" model 12 spectrometer operated in the continuous ionization mode. Spectra were recorded on an X-Y recorder. Spectra obtained were compared with data published by the American Petroleum Institute. Spectra were almost identical, the major difference being that the "Time-of-Flight" gave a larger molecular ion peak.

Paraffins identified included n-C₂₁H₄₄, 2-methyl-C₂₁H₄₃, n-C₂₂H₄₆, 2-methyl-C₂₂H₄₅, n-C₂₃H₄₈, 3-methyl-C₂₃H₄₇, n-C₂₄H₅₀, 2-methyl-C₂₄H₄₉, n-C₂₅H₅₂, 3-methyl-C₂₅H₅₁, n-C₂₆H₅₄, 2-methyl-C₂₆H₅₃, n-C₂₇H₅₆, 3-methyl-C₂₇H₅₅, n-C₂₈H₅₈, 2-methyl-C₂₈H₅₇ and n-C₂₉H₆₀.

SIGNIFICANCE OF RECENT RESEARCH ON GRAPEFRUIT FLAVONOIDS

by

R. F. Albach
Southern Utilization Research and Development Division
U.S. Fruit and Vegetable Products Laboratory
Weslaco, Tex.

Several decades ago it became apparent that due to the increasing production of grapefruit in the United States and the rise of the citrus processing industry, a need existed to learn more about the chemical composition of grapefruit and to determine its influence on processing characteristics and product quality.

The earlier research on grapefruit composition was directed mainly toward finding useful byproducts in citrus waste, from whose sales the processing industry, and, indirectly,

the grower, would receive larger returns on their capital investments. Pectin production from waste peel is an example of such a byproduct.

Isolation of the flavonoids from waste pulp also has received much attention; and the earlier work on flavonoid composition of grapefruit was primarily directed toward its importance as a potential byproduct.

More recently, processors, food scientists, and chemists have shown increasing

^{1/} Mr. Brogden terminated his employment at the Fruit and Vegetable Products Laboratory shortly before the Conference.

interest in the effect of the flavonoids in grapefruit on the quality of juice and other consumer items such as fruit sections and salad packs. Although the mild bitterness which is associated with grapefruit is a distinctive and desirable quality which is found appealing to most customers, an excess of bitterness is generally considered unpleasant.

While fresh grapefruit sales may not suffer appreciably from occasional cases of excessive bitterness, this same quality is less likely to be tolerated by the consumer of a processed product since he expects, and is entitled to, a higher degree of quality control. If such a dissatisfied consumer was only trying the grapefruit product for the first time or was only an occasional purchaser, he may think that all other processed grapefruit products, regardless of brand, are similar, and decide never to give them a second try.

It has been just over a hundred years since DeVry (2) isolated a material from Pumelo flowers which was found to be extremely bitter. Another chemist, Hoffman (5), named this compound naringin, after the Sanskrit word "naringi", meaning orange. Naringin was later found to be the principal bitter component of the grapefruit as well. Although naringin had been known for more than a hundred years and was of some economic importance, it was only three years ago that Horowitz and Gentili (8), at the Fruit and Vegetable Chemistry Laboratory in Pasadena, completed the work started three generations ago, and established conclusively the structure of naringin.

We at the U. S. Fruit and Vegetable Products Laboratory in Weslaco, Texas, first became acutely aware of the bitterness problem in 1953 while developing a process of pulp fortification for the juice of red-fleshed grapefruit (9). The amount of pulp which could be added to enhance the red color of the juice (and incidentally, to raise the juice yield) was limited by a corresponding increase in bitterness. Although ways have been found to avoid the bitterness effect in the pulp fortification process, a higher degree of control analyses and processing costs are incurred which lessens the economic advantage of the method.

In order to evaluate the effect of pulp fortification on bitterness, a large number of colorimetric chemical tests were run for the analysis of naringin. It became apparent that the existing quantitative and semiquantitative tests for naringin gave inadequate correlation with subjective taste evaluations of bitterness.

It was not known at the time what was responsible for the anomaly; the tests, the concept of naringin being the only bitter component in grapefruit, or the sensory evaluation.

The most convenient and widely used test for flavanones in grapefruit had been that of Davis (1), which measured the yellow color produced by flavanones in alkaline diethylene glycol. Horowitz and Gentili (6) have pointed out the limitations of the Davis test and have suggested that the poor correlation with bitterness during a given season was due to the natural hydrolysis of naringin to prunin in the fruit.

Grapefruit was soon found to contain two additional bitter flavonones which were not adequately determined by the Davis test. These were poncirin, found by Horowitz and Gentili in the peel in 1961 (7), and neohesperidin, found by Dunlap and Wender in 1962 (3).

In order to provide a more thorough understanding of the flavonone composition of grapefruit and its relationship to maturity, the United States Department of Agriculture established a research contract with the University of Oklahoma Research Institute (Contract No. 12-14-100-6879(72)). The principal investigator was S. H. Wender. He was assisted by W. J. Dunlap and two doctoral candidates: R. E. Hagen and J. W. Mizelle. F. P. Griffiths of the Weslaco laboratory was the USDA technical representative on the contract.

The Oklahoma group, working with the segments of Texas-grown Ruby Red grapefruit, have confirmed the existence of naringin, poncirin, and neohesperidin in these segments. Accompanying these three bitter neohesperidosides were the three corresponding nonbitter rutinoides, naringenin 7-rutinoides, isosakuranetin-7-rutinoides, and hesperidin (11).

Two research tools of possible wider usefulness in the study of flavonoid compounds have resulted from this research. These are: column chromatography with nonaqueous solvents on polyvinylpyrrolidone powder and the use of polyamide thin layer chromatographic plates with nitromethane-methanol developing solvent. These chromatographic procedures give remarkable separations of very similar flavonone compounds. The systems were developed together, with the aid of personnel from the Weslaco laboratory.

Besides the six flavanones already mentioned as being present in the segments, two additional compounds were isolated in small yield which were respectively identical to naringin and naringenin-7- β rutinoid in all physical determinations attempted, except for their different rate of migration on the polyvinylpyrrolidone column. It was speculated that these two compounds were possibly diastereoisomers of naringin and naringenin-7- β rutinoid. However, sufficient quantities of the two compounds were not available to test this hypothesis.

It can be seen from the variety of flavanones which are found in grapefruit segments that a departure of Davis test values from observed bitterness can be rationalized in both directions. A low Davis value relative to bitterness could be due to the presence of the bitter poncirin and/or neohesperidin which gives low Davis values but some bitterness. A high Davis test and low bitterness could be due to the preponderance of the non-bitter naringenin-7- β rutinoid.

Since none of the previously described quantitative methods were capable of differentiating between the flavanones of grapefruit, it was necessary for the Oklahoma group to develop a new scheme of analysis (4).

The method involves a preliminary quantitative isolation of the flavonoids from the sample by use of hot alcoholic washes and filtration. The concentrated filtrate is then chromatographed on a polyvinylpyrrolidone column. The fractions obtained are concentrated and aliquot portions are spotted on polyamide plates along with standards. The plates are developed with nitromethane-methanol as irrigant. After development is complete the portion of the adsorbent containing the individual compounds is removed. The flavonoids are washed off the adsorbent

with methanol by use of a microfiltration apparatus. The filtrate is collected in a volumetric flask. Aluminum chloride is added and the solution is brought to volume. The concentration of the flavanone is obtained by measuring the fluorescence of the solution in a fluorometer and then comparing the value obtained with that of the standards. As one can see by the complexity of the procedure, this method is not likely to find much acceptability in a quality control laboratory. However, it is useful in research.

By the use of this method, the Oklahoma group has obtained a standard error of 1.2 percent for naringin determinations. The standard errors for naringenin-7-rutinoid and poncirin are about 2.4 percent.

Table 1 illustrates some results of an analysis on juice sacs of fresh fruit and some canned from another season and source. It can be seen that in both cases the naringenin-7-rutinoid has a concentration of 40 percent of that of naringin.

Table 1. --Analyses for flavanone glycosides in juice sacs of Texas Ruby Red grapefruit and in Texsun brand canned grapefruit juice.

Compounds	Concentration in juice sacs (μ g./g.) wet weight	Concentration in juice (μ g./ml.)
Naringin	546	306
Naringenin rutinoid	210	124
Poncirin	20.6	17.0
Isosakuranetin rutinoid	6.4	5.3
Neohesperidin	24.6	10.5
Hesperidin	13.0	9.9

1/ Table taken from Hagen, R. E., Dunlap, W. J., Mizelle, J. W., Wender, S. H., Lime, B. J., Albach, R. F., and Griffiths, F. P. Anal. Biochem. 12, 472 (1965).

The Oklahoma group has recently completed a seasonal study on the concentration change of the individual flavanones in Texas Ruby Red grapefruit. Analyses were run on groups of grapefruit picked at monthly intervals from September through April. All six of the known flavanones in grapefruit appeared to be decreasing in concentration at approximately the same rate at any given time. The rate of decrease was greatest in

the early season and became progressively less marked as the season progressed; until in the very late season there was very little change between consecutive months.

The fact that the flavanone-7-rutinoside and flavanone-7-neohesperidoside concentrations both decreased at the same rate, indicates that transrhamnosidation did not appear to occur. It had been suggested that such transglycosidation may have been responsible for the decrease in bitterness of grapefruit as the seasons progressed.

When results from Davis tests were compared with results from fluorometric analysis on the same samples it was observed that the Davis tests results were consistently greater than the sum of the fluorometric results for naringin and naringenin-7-rutinoside. However, the Davis test results, although high, paralleled quite closely the change in total concentration of naringenin glycosides as the season progressed. The Davis test thus appears to give a very good relative indication of the presence of these naringenin derivatives.

It has often been observed that in the late season the bitterness of grapefruit decreases quite rapidly. The data from the University of Oklahoma Research Institute study indicates that the flavanones do not undergo any dramatic disappearance or interconversion at that time. This may suggest the importance of other factors being involved in juice bitterness.

Recent research, at the Weslaco laboratory, with isotopic labeling of growing grapefruit during different seasons of the year has indicated that the time of flavanone formation or translocation in the fruit may be confined to the very early season. This would be consistent with the observations of Kesterson and Hendrickson (10) who found that the amount of naringin per fruit did not increase significantly after the fruit reached a diameter of about two inches.

The unavailability of pure citrus flavanones in sufficient quantities to conduct meaningful experiments has hampered the attainment of a full understanding of their chemical, enzymatic, and organoleptic properties. Our laboratory has undertaken the preparation of quantities of grapefruit flavanones for use in our studies on enzymatic

and resin debittering, organoleptic relationships, and for development of simple, specific quantitative tests.

In an attempt to find better sources of the grapefruit flavanones, a survey of different citrus species, hybrids, and close relatives was conducted. The fruits of several dozen varieties for this survey were supplied by E. O. Olson of the Crops Research Division, Weslaco. Besides providing clues to better source material, plant breeders and taxonomists would also find the results of this survey useful in their work.

Extracts of the whole fruit were analyzed by thin-layer chromatography. Each species and many hybrids appeared to yield a pattern of component spots on the TLC plate which was characteristic of certain species. The presence of flavanone spots was inferred from simultaneous chromatography with standards and from the characteristic fluorescence produced after spraying with aluminum chloride solution. Although this alone is inadequate chemical proof of the presence of a particular flavanone compound, if the pattern of spots is interpreted with due regard to published data involving adequate chemical structure proof of components, then reasonable inferences can be drawn which aid in designing more definitive investigations.

Figure 1 illustrates the patterns of compounds more or less typical to the particular species indicated. Those spots with vertical lines are inferred to be flavanones. The positions of six flavanones definitely found in Citrus paradisi are indicated. Of these six flavanones, C. reticulata appears to have only the three rutinosides and C. grandis shows only naringin, a neohesperidoside, to be present in significant quantity. It had been theorized that C. paradisi may be a hybrid of C. reticulata and C. grandis. The flavanone pattern of these species would be consistent with this proposal since grapefruit contains nothing which is not found in either of the two suspected parents.

We are currently examining the flavanone pattern of some of the known hybrids of the various citrus species. This may lead to a better understanding of the inheritance of citrus flavanones and ultimately may

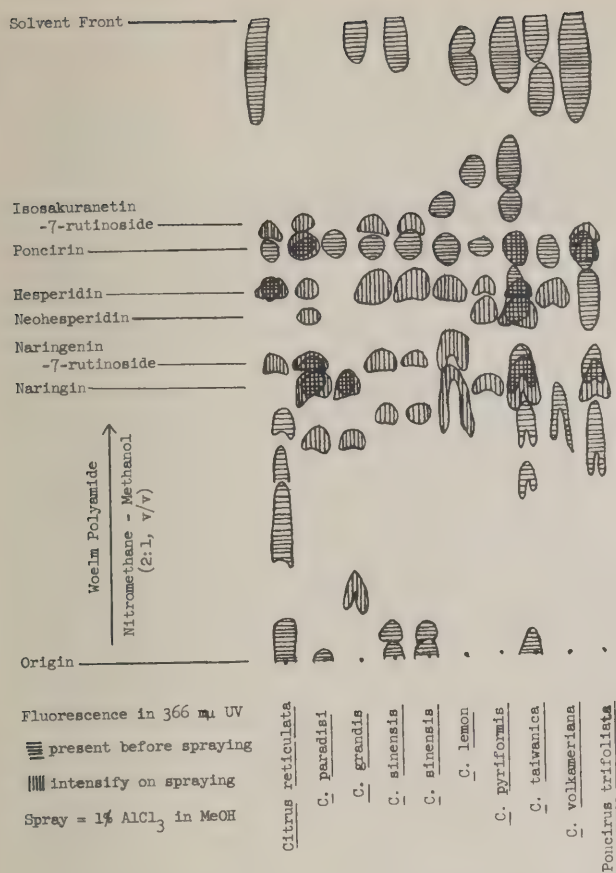


Figure 1—Significance of recent research on Grapefruit Flavonoids

be useful in breeding citrus varieties containing a more desirable flavanone composition. Other classes of flavonoid compounds also are being examined.

REFERENCES

1. Davis, W. B., Anal. Chem. 19, 476 (1947).

2. DeVry, F., Jahresber, Pharmakognosie, 134 (1866).
3. Dunlap, W. J., and S. H. Wender, Anal. Biochem. 4, 110 (1962).
4. Hagen, R. E., W. J. Dunlap, J. W. Mizelle, S. H. Wender, B. J. Lime, R. F. Albach, and F. P. Griffiths, Anal. Biochem. 12, 472 (1965).
5. Hoffman, E., Arch. Pharm. 214, 139 (1879).
6. Horowitz, R. M., and B. Gentili, Food Res. 24, 757 (1959).
7. Horowitz, R. M., and B. Gentili, Arch. Biochem. Biophys. 92, 191 (1961).
8. Horowitz, R. M., and B. Gentili, Tetrahedron 19, 773 (1963).
9. Huffman, W. A. H., B. J. Lime, and W. C. Scott, Proc. Rio Grande Valley Hort. Inst. 7, 102 (1953).
10. Kesterson, J. W., and R. Hendrickson, "Naringin, A Bitter Principle of Grapefruit," Bulletin 511, University of Florida Agricultural Experiment Station, Gainesville (1953).
11. Mizelle, J. W., W. J. Dunlap, R. E. Hagen, S. H. Wender, B. J. Lime, R. F. Albach, and F. P. Griffiths, Anal. Biochem. 12(2), 316 (1965).

DISCUSSION

Question: Was Rangpur lime in your study?

R. F. Albach: I'm not a taxonomist. (Help from audience - No.)

SESSION II

R. W. Kilburn, Chairman

NEW GRAPEFRUIT CONSTITUENTS AND THEIR IMPORTANCE

(SUMMARY)

by

E. A. Beavens, V. P. Maier, and W. D. MacLeod
Western Utilization Research and Development Division
Fruit and Vegetable Chemistry Laboratory
Pasadena, Calif.

(Presented by E. A. Beavens)

Limonoid bitter principles, particularly limonin, occur in a number of citrus fruits, mainly in the seeds, albedo, center core, segment membranes, and even in the walls of juice sacs. During processing and storage these bitter principles pass into the juice in amounts sufficient to cause bitterness unacceptable to the consumer. Bitterness is not apparent in freshly extracted juice but becomes so after a few hours at room temperature or within a few minutes if the juice is heated. Delayed bitterness is best explained on a physical basis. Initially, limonin is present in the juice as a constituent of the tissue fragments that make up the suspended solids. Because of its slow solubility, it takes time for the limonin to diffuse from these fragments into the juice and to reach a concentration sufficiently high to make the juice taste bitter. Heating speeds up the rate of solubility.

In general, the limonin content of citrus fruits decreases with advancing maturity. With most varieties it disappears, at least in the endocarp, by the time the fruit reaches optimal maturity. However, some varieties such as the navel and Shamouti oranges, retain significant amounts of the bitter principles at normal maturity, so bitterness in the juice becomes an important practical problem. Investigations of bitterness in citrus products have been hampered by the absence of a satisfactory method of assay. The development of such a method is now more feasible since the structure of limonin was worked out in 1960. It was shown to be a tri-terpenoid oxidation product containing

two lactone rings, one ketone group, one furan ring, and two cyclic ether groups. A method of analysis has been proposed by Chandler and Kefford^{1/} in Australia. The Pasadena Laboratory has a research contract with the Stanford Research Institute to develop a practical method of analysis for limonin.

Acidity of the juice will influence limonin bitterness in that it will be accentuated in juices of higher acidity. Because of the recognized effects of acidity and sweetness on subjective responses to bitterness it may be difficult to establish a consistent relationship between limonin content and organoleptic assessments of bitterness in juice products. The bitterness problem is further complicated by the fact that other bitter constituents may be present in citrus juices such as naringin, obacunone, nomilin, limonexic acid and several still unknown substances.

The bitterness of grapefruit juice has been ascribed to certain flavonoid glucosides, particularly naringin. Workers at the Pasadena Laboratory now have shown that limonin also occurs in grapefruit juice at levels above its taste threshold. It was present in all samples examined which included commercial single strength juice, frozen concentrate, crater-dried powder, and laboratory prepared juice and pulp samples from grapefruit grown in California, Arizona, Florida, and Texas. To confirm these results limonin was isolated in crystalline form from a

1/ "Chemical Assay of Limonin, The Bitter Principle in Oranges" by B. V. Chandler and J. F. Kefford. In press.

large batch of commercial grapefruit concentrate and from laboratory extracted grapefruit juice. The crystalline limonin was identical in all respects with an authentic sample, i. e., IR, m. p., R_f values, color reactions and taste. Limonin was found by isolation to occur in the grapefruit concentrate in amounts up to 9.5 p. p. m. on a reconstituted juice basis. Therefore, it was present in sufficient quantity to contribute to the overall bitterness of grapefruit juice.

All samples of grapefruit tested were mid- and late-season fruit. The presence of limonin in late season fruit is especially significant because with navel oranges the limonin content decreases with maturity. In the late-season grapefruit tested, limonin was still present six months after the fruit had reached commercial maturity. Apparently, limonin persists longer in grapefruit than it does in the navel orange.

Little is known about the polyphenolic compounds in grapefruit, particularly those present in the endocarp or edible portion of the fruit. A more complete picture of the polyphenolic content of grapefruit endocarp might be useful in solving certain biochemical, pharmacological and technological problems. One such problem is the bitterness imparted to grapefruit juice by excessive amounts of naringin. Information on the presence of other polyphenols in grapefruit and the nature of the biosynthetic pathways leading to the accumulation of naringin might lead to a solution of this bitterness problem.

Enzyme hydrolysis of extracts of grapefruit endocarp indicated the presence of twelve principal polyphenols as follows:

Flavanones-naringenin, isosakuranetin, hesperetin

Flavone-apigenin
Flavonal-kaempferol
Psoralen-bergaptol
Coumarins-umbelliferone and scopoletin
Cinnamic acids-para coumaric, caffeic and ferulic
Trihydroxyphenol-phloroglucinol

Chromatographic comparison of extracts of grapefruit endocarp before and after hydrolysis showed, that with the exception of bergaptol, all of these compounds occur primarily in bound forms such as glycosides and esters. Thus, these twelve polyphenolic moities could indicate the presence of many times more that number of naturally occurring derivatives in the fruit. The presence of 25-30 fluorescent compounds in the chloroform-soluble fraction of grapefruit endocarp is further evidence of the complex composition of this fruit. Chromatographic analysis of the polyphenolic hydrolysis products of grapefruit peel showed that it is similar to but less complex than that of the endocarp. The biggest difference is the higher concentration of naringin in the peel.

The bicyclic, conjugated, sesquiterpene, ketone, nootkatone, was previously reported at one of these conferences to be present in grapefruit peel oil and in peel-oil-free grapefruit juice. The flavor intensity of grapefruit oil appears to be related to the relative abundance of nootkatone. Commercial flavor chemists have described nootkatone as being the predominant flavoring constituent in grapefruit oil similar to the role of citral in lemon oil. In addition to its previous identification by IR spectra and melting point of its 2,4-dinitrophenylhydrazone derivative, nootkatone has been confirmed by its absolute configuration, stereochemistry, and structure. Final proof will be its synthesis which is now in progress.

A REVIEW OF PROCEDURES FOR PRODUCTION OF GRAPEFRUIT CRYSTALS USING THE CRATER-TYPE FOAM-MAT DRYER

(SUMMARY)

by

R. E. Berry, O. W. Bissett and C. J. Wagner, Jr.
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by R. E. Berry)

During the past year, the "crater-type" form-mat dryer installed in the pilot laboratory has been used for the production of both orange and grapefruit powders. Extensive experiments have been carried out on grapefruit powders, and the conditions for processing grapefruit concentrate to form dehydrated juice crystals have been developed to a practical point.

Methods for foaming grapefruit concentrate have been developed using an eight-inch high speed mixer. Where formerly as much as 1.5 percent foaming agent had been required for the production of a satisfactory grapefruit foam, the technique has now been developed to a point where only about 0.45 percent additive is required.

In the procedure for drying, it is now possible to produce crystals of about 1.0 percent moisture content, using temperatures such that the product temperature never exceeds 170°F. For most concentrates, drying at temperatures of about 150 to 160°F. for about 9 to 10 minutes followed by about 1 to 2 minutes at 160 to 170°F. is sufficient to produce crystals of moisture content sufficiently low that the product does not "cake" under normal usage and has a practical storage life.

A procedure has been developed which enables the increase of powder bulk density from about 0.3 g./cc. to about 0.8 g./cc., using cold compression, i.e. with the use of mechanical pressure and without heat or added release agent. This makes it possible to achieve more practical bulk density without impeding solubility. Comparison of solubility of foam-mat grapefruit crystals prepared in

this manner with several different synthetic materials, "instant" drinks, and pure sucrose, revealed very little difference in solution time in 40°F. water.

Using a packaging procedure which includes evacuation and packaging under carbon dioxide atmosphere, the shelf life of these crystals, as well as the appearance of the reconstituted product, and the flavor have been enhanced.

DISCUSSION

Question: What is your standard solution-time technique?

R. E. Berry: Normally, we first measure out the proper amount of 40°F water. Then one man drops the material in the water and begins stirring. Another man starts the stopwatch and then both of them watch it. When, in the opinion of both it is completely dissolved, they stop the stopwatch and record the time.

Question: Do you use a spoon for stirring?

R. E. Berry: Yes, we try to do what a consumer would naturally do.

Question: Are you using any flavoring material in your grapefruit now?

R. E. Berry: Yes, we use commercial Per-mastable "locked-in" oil.

DEHYDRATION OF CITRUS JUICES

by
J. H. Nair
Research Consultant
Raleigh, N. C.

The preservation of orange and lemon juice by dehydration has been the objective of a vast amount of research effort for decades. There is no need, with this audience, to adduce at length the many reasons which contribute to make the goal of an easily soluble, long-keeping powder retaining the natural flavor and aroma of fresh citrus juice an elusive will o' the wisp. My own acquaintance with these problems began some forty-five years ago when I started studies of some of the physical-chemical aspects of spray dehydration then being applied by the research staff of Merrell-Soule Company to a broad spectrum of natural products. Through the intervening years I have had the opportunity to work with several dehydration systems, such as are illustrated in Figure 1. These included vacuum chambers, spray towers, tray tunnel dryers, belt dryers, vacuum freeze dryers, and vacuum belt dryers. So I have managed to acquire considerable knowledge and experience with

what can and cannot be accomplished in preserving various foodstuffs by desiccation. At Merrell-Soule Company in the 1920's our experimental work covered the juices of tomato, grape, apple, cherry, raspberry, loganberry, blackberry, orange, lemon, grapefruit, tangerine, plum, pear, peach, nectarine, lime, apricot, pineapple and probably others which I do not recall. We operated with a small, commercial Merrell-Soule drying chamber, having a Cottrell electric precipitator for recovery of solids from the effluent air-stream. Trial batch size ran between 25 and 50 gallons. In practically all cases we succeeded in recovering dry solids of low moisture content and good flavor which stood up well for various lengths of time when packaged in sealed tins, sometimes in air and sometimes under carbon dioxide or nitrogen. Such products as the berry juices, pineapple, grape, and the blander fruits were quite soluble and palatable after 10 years at room temperatures without additives.

The commercial application of such a pressure spray drying system with concurrent air flow was impeded by the development of a glazed coating of dry product after an hour or so of operation, due to the combination of high humidity and hot wall surfaces with juices relatively high in sucrose content. Eventually a partial solution of this problem was effected by combining the juices with low-dextrose-equivalent corn syrup, although this diluted the natural flavor and made the powders unsuitable for beverage purposes. Nonetheless, a strong patent was obtained for the process and large tonnages of powdered orange and lemon juice have been manufactured by this method for the past forty years and sold very profitably by Merrell-Soule and Borden and, in later years, by others, to the ice cream, bakery and dessert segments of the food industry. Due to the fineness of particle size such powders alone are difficult to dissolve in cold or room temperature water. When mixed with cane sugar the lemon powder in particular makes a most satisfactory lemonade and for a number of years, Merrell-Soule Co. sold considerable quantities of it

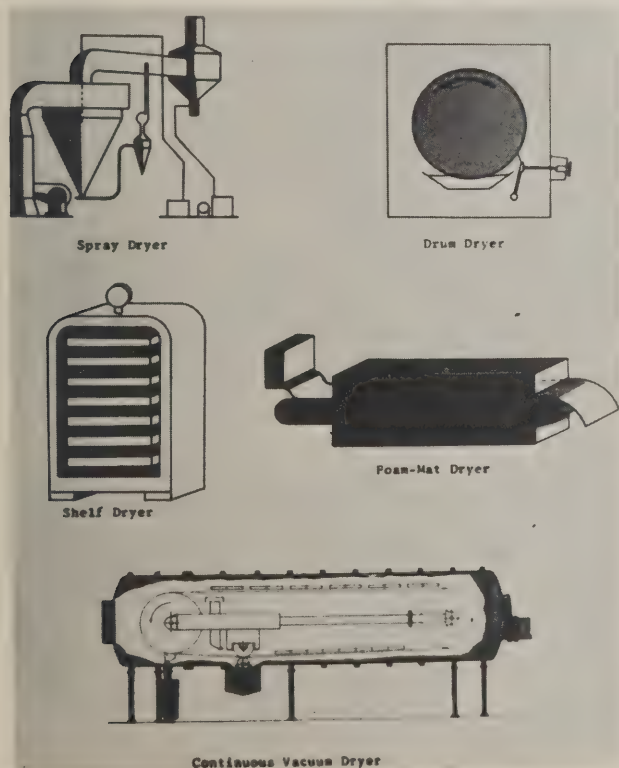


Figure 1.—Types of dryers

to the retail trade. When Borden took over Merrell-Soule in 1928 they phased out this small volume business rather quickly.

The development of the vacuum belt dryer (Figure 2) by the Chain Belt Co. made it

The first commercial installation of such a dryer was made at Plant City, Fla. some 15 years ago. Figure 3 gives a view of this installation and Figure 4 shows the multiple steam ejector system which maintains the required vacuum and carries off the condensed

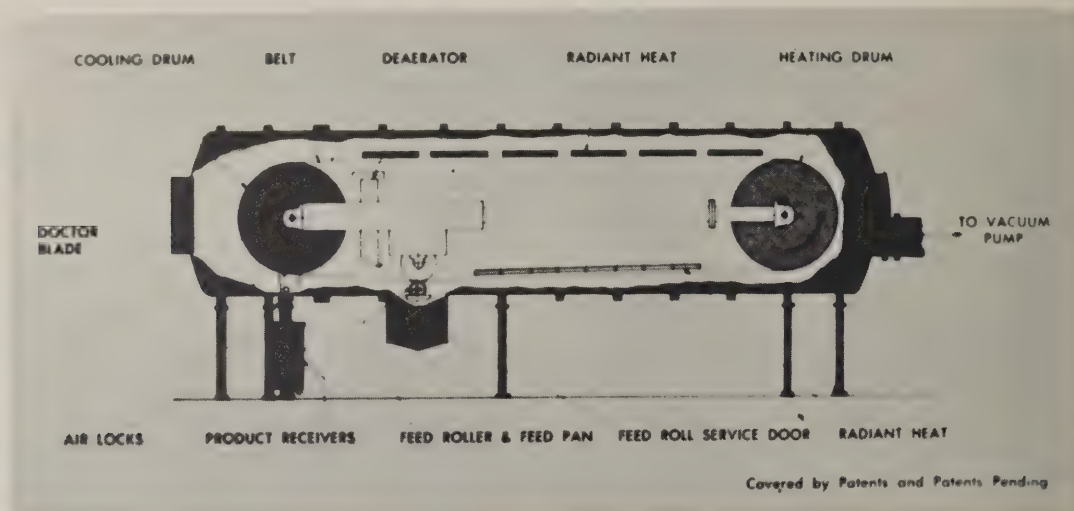


Figure 2.—Vacuum belt dryer (schematic).

possible to dehydrate high sucrose juices commercially. This audience is familiar, I expect, with the operation of this system. A viscous concentrate of the juice is picked up by an auxiliary roll and transferred in a thin layer to the under side of a 48" endless stainless steel belt, moving counterclockwise over rolls, in a 50 ft. cylindrical chamber maintained under a vacuum of about 7 mm. Banks of steam-heated coils radiate heat to the upper surface of the belt and the sudden reduction in pressure causes the concentrated juice to expand or puff up slightly as it is deposited on the moving surface, a useful aid for rapid drying. The belt moves over a large, steam-heated roll at one end of the chamber and then passes between banks of electric heating elements, during which stage moisture is reduced to about 2 percent residual. The belt then passes over a refrigerated roll at the opposite end of the chamber, where the dried juice is cooled before being scraped off the surface by a doctor knife. The coarse flakes are conveyed transversely in a trough below, filled with a reversible screw, to one of two exit ports connected to a drum. When filled the drum is withdrawn by closing off a vacuum lock.

water vapor. This equipment has been used to produce orange crystals, grapefruit crystals, and some lemon crystals, for which the biggest outlet has been the Armed Forces. Since this installation was made several of these dryers have been purchased by various companies for drying tea extract and one has been installed in South America for dehydrating citrus and tomato juices.

Tables 1 through 6 portray pertinent economic data on vacuum belt drying of these two liquids. In table 1 are shown the required process conditions, while table 2 gives the utility requirements. Utility and labor cost factors are seen in table 3, and yearly time allocations appear in table 4. A summary of yearly costs for both products are shown in table 5. Table 6 presents a comparison of the various quality characteristics of tomato juice dried by various processes. It will be observed that vacuum belt drying leads to the best overall dried product.

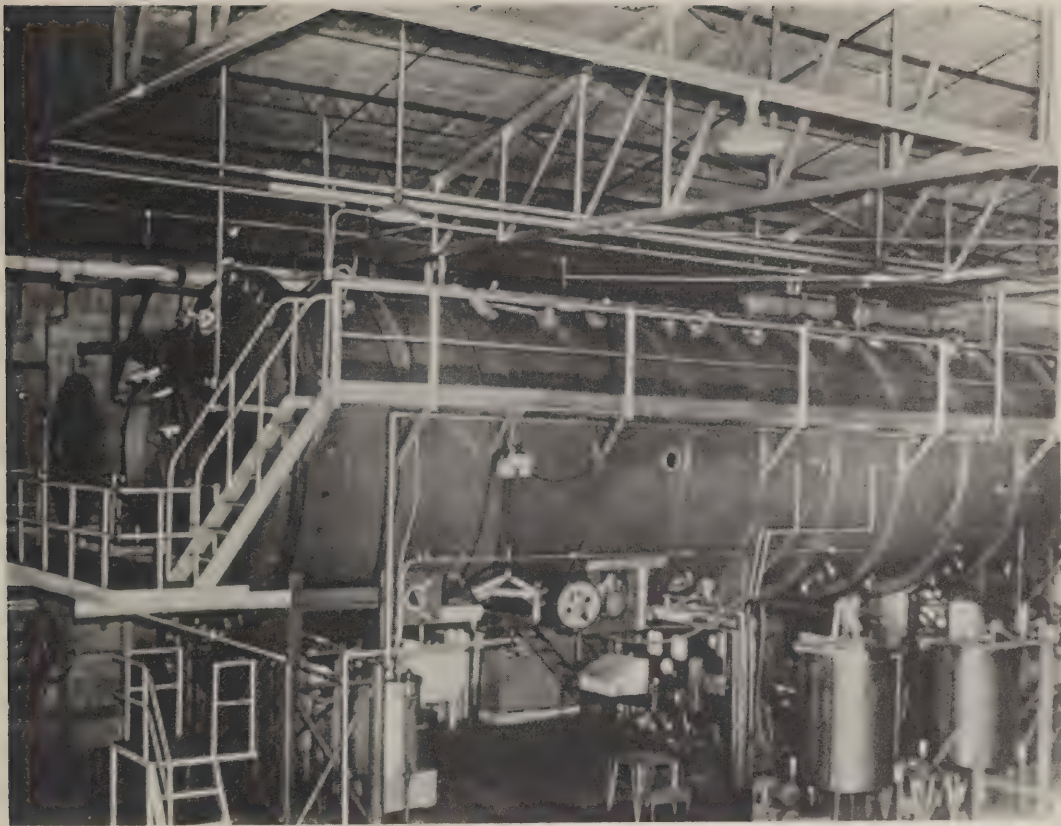


Figure 3.—Vacuum belt dryer (commercial installation).



Figure 4.—Multiple steam ejector system.

Table 1. --Process conditions for continuous vacuum dehydration of juice

Process condition	Unit	Juice	
		Orange ¹	Tomato ¹
1. Production rate	lb./hr.	400	400
2. Feed concentration	percent solids	60	32
3. Feed rate	lb./hr.	667	1,250
4. Evaporation rate	lb./hr.	267	850
5. Dryer pressure	mm. Hg abs.	1.5	3.5
6. Belt speed	f. p. m.	60	74
7. Belt temperature heated	°F.	165	214
8. Belt temperature cooled	°F.	55	62
9. Cooling drum temperature	°F.	15	20

^{1/} Pilot plant data.

Table 2. --Utility requirements for continuous vacuum dehydration of juice ^{1/}

Utility	Purpose	Unit	Juice	
			Orange	Tomato
Steam-115 p. s. i. g.	Ejectors ^{2/}	lb./hr.	4,635	5,400
Steam-115 p. s. i. g.	Evaporation	lb./hr.	285	920
Steam-115 p. s. i. g.	Heating belt	lb./hr.	177	313
Steam-115 p. s. i. g.	Radiation losses	lb./hr.	-	17
Steam-115 p. s. i. g.	Radiant heaters	lb./hr.	170	472
	Total steam	lb./hr.	5,267	7,122
Water-85° F.	Cooling drum ^{3/}	g. p. m.	240	240
Water-85° F.	Ejector condensers ^{2/}	g. p. m.	1,100	1,250
	Total water	g. p. m.	1,340	1,490
Electricity	Motors, refrigeration, etc.	kw.	143	143
	Radiant heaters	kw.	75	120
	Total electricity	kw.	218	263

^{1/} Unpublished data from chain belt company.

^{2/} Data from ejector manufacturer.

^{3/} Data from refrigeration equipment manufacturer.

Table 3. --Utility and labor cost factors

Cost factors	Unit	Cost per unit (Dollars)
Steam	1,000 lb.	1.00
Water-Cooling tower	1,000 gal.	.01
Water-10 percent makeup	1,000 gal.	.10
Electricity	kw. -hr.	.01
Operator's labor rate	hr.	2.25
Maintenance personnel	hr.	4.00

Table 4. --Time allocation based on 6,700 hr./yr. total operation

Operation items	Time Hr./yr.
Production time (24 hr./day-5 days/wk. 50 wk./yr.)	6,000
Cleanup and maintenance	700
Labor-operators	6,700 ^{1/}
Labor-maintenance	700 ^{1/}
Steam (includes 2 hr./wk. chamber evacuation)	6,100
Water	6,100
Electricity	6,100
Electrical radiant heat	6,000

^{1/} Man-hr./yr.

Table 5. --Summary of dollar costs per year for continuous vacuum dehydration of juice

(yearly production of 2,400,000 lb.)		
Cost factor	Juice	
	Orange Dollars	Tomato Dollars
Labor	17,875	17,875
Steam	32,129	43,444
Water	9,784	10,907
Electricity	13,223	15,923
Equipment at 10 pct./yr.	32,000	32,000
Maintenance supplies	3,000	3,000
Installation 10 pct./yr.	3,000	3,000
Cost per lb., solids	.0463	.0526
Cost per lb., water removed	.0693	.0247
Cost per lb., of feed	.0277	.0168

Table 6. --Comparison of types of dryers for tomato juice powder

Type of dryer	Present application	Additives required	Solubility	Hygroscopicity	Product uses	Shelf life	Facility
Vacuum shelf dryer	Pilot plant	None	Excellent	Hygroscopic	Research	Good	WURDD ^{1/}
Drum dryer	Commercial	None	Fair	Slightly hygroscopic	Condiments and soups	Unknown	
Spray dryer	Pilot plant	None	Poor	Slightly hygroscopic	Condiments and soups	Unknown	
Foam mat dryer	Pilot plant	Approx. 1% mono-glyceride	Fair	Moderately hygroscopic	Process evaluation	Unknown	WURDD ^{1/}
Continuous vacuum dryer	Pilot plant	None	Excellent	Hygroscopic	Beverage, condiments, soups	Good	Chain Belt Co., Milwaukee, Wis.

^{1/} Western Utilization Research and Development Division, USDA, Albany, Calif.

About 10 years ago staff members of the Western Regional Research Laboratory of the U. S. Department of Agriculture conceived of a method of puffing or foaming juice concentrates when these were extruded and deposited on a tray or a moving surface. The system has been materially improved through continued experimentation during the inter-

vening years and its present status has been well presented by the preceding speaker, Dr. Berry. I will not take time to discuss it further other than to point out that it is not applicable to straight citrus juices, since a surface-active agent must be added to create the "craters" or foam essential for rapid drying.

Rather similar in principle is the dehydration system termed "microflake belt drying." This is an adaptation of equipment employed in the tobacco industry for many years for converting homogenized tobacco dust into a flake form suitable for incorporation in cigarettes. A solid stainless steel belt, 4 to 8 feet wide, and from 100 to 200 feet in length, serves to convey a foamed concentrate, extruded onto its surface, through a drying zone. Heated steam coils below the belt heat its surface, while heated air at 170°-190° F. is blown over the top of the extruded droplets in a manner similar to the one now adapted for "crater" drying. The dried product continues on the belt into an air-conditioned room where it is cooled before being scraped off with a doctor knife. The fine flakes of citrus or tomato can be packaged directly in this low-humidity room or conveyed to a separate packaging area. The resultant products retain their original color, flavor and aroma to a considerable degree, satisfactory for beverage purposes, with a minimum of heated flavor. No commercial installation of this microflake process has been made to date, so far as I know.

This brings us to vacuum freeze dehydration and we could well spend an entire afternoon in discussion of this rapidly-expanding system of drying heat-sensitive food materials. Figure 5 gives a view of a commercial layout with equipment developed by FMC Corporation. This is being used today for instant coffee (Maxim) and for drying berries and other fruits in Oregon. Figure 6 shows the Vickers system in diagrammatic form. An installation of this equipment has been made at Irish Sugar Co. in Mallow. This is the so-called "AFD" or accelerated freeze drying method worked out by the British Ministry of Agriculture, Fisheries and Food at its Experimental Factory in Aberdeen, Scotland. Another type of Vickers equipment is being used for instant coffee by Brooke Bond, Ltd. in England.

Freeze dehydration of natural materials is a fairly old technique. It has been used for 30 years to preserve biological materials, such as blood plasma, antibiotics, bacterial cultures and histological sections. The first commercial application to foods in this country began with an operation by Wager in 1954 in Texas for drying whole shrimp. In Europe a year later Hartog's Fabrieken in

Holland initiated the production of freeze-dried chicken dices. By 1960 a considerable volume of dried products of various kinds was being processed in the United States. Each year since then the installed freeze-drying capacity has about doubled in size, an estimated 57,000 sq. ft. of usable shelf area being available at the end of 1964. This equipment could handle approximately 55,000 tons of raw food material per year, though perhaps 1/4 as much was put through the freeze dryers last year. Some 30 companies are now doing commercial freeze drying. A broad range of lyophilized foods are now to be found in the market place.

There has been a gradual evolution in equipment design, starting from conventional vacuum cabinets or chambers so modified as to provide a water vapor trap between chamber and exhaust pump, plus a circulating hot liquid in hollow shelves to supply the heat to maintain sublimation, and tight enough conditions to attain absolute pressures below 1 torr. Early commercial freeze dryers for food, built by Atlas A/S, of Copenhagen, employed multiple steam jet ejectors in series. These systems have the virtues of simplicity, low investment and maintenance costs, and combined exhaustion on noncondensibles and water vapor. Operating costs for utilities is high, however. Today, general practice is to employ oil-sealed rotary or vane pumps, with air ballasting or the Roots pump in combination with a single-stage rotary backing pump. Sometimes combinations of steam jets and mechanical pumps are used.

Direct-expansion refrigerated condensers are used with mechanical pumps for freezing out the water sublimed from the drying product. Resistance to vapor flow can be minimized by locating the condenser on the inside walls of the chamber, as has been done by FMC Corporation. Such a design has the handicap that the entire vessel is out of operation during the period required for de-icing of the plates. More conventionally, the condensers lie outside of the vacuum chamber proper, but are connected to it by quite large diameter pipes.

Until recently all freeze-drying equipment employed hollow shelves or platens on which were positioned numerous small trays carrying the frozen material to be lyophilized. In one case these platens are carried

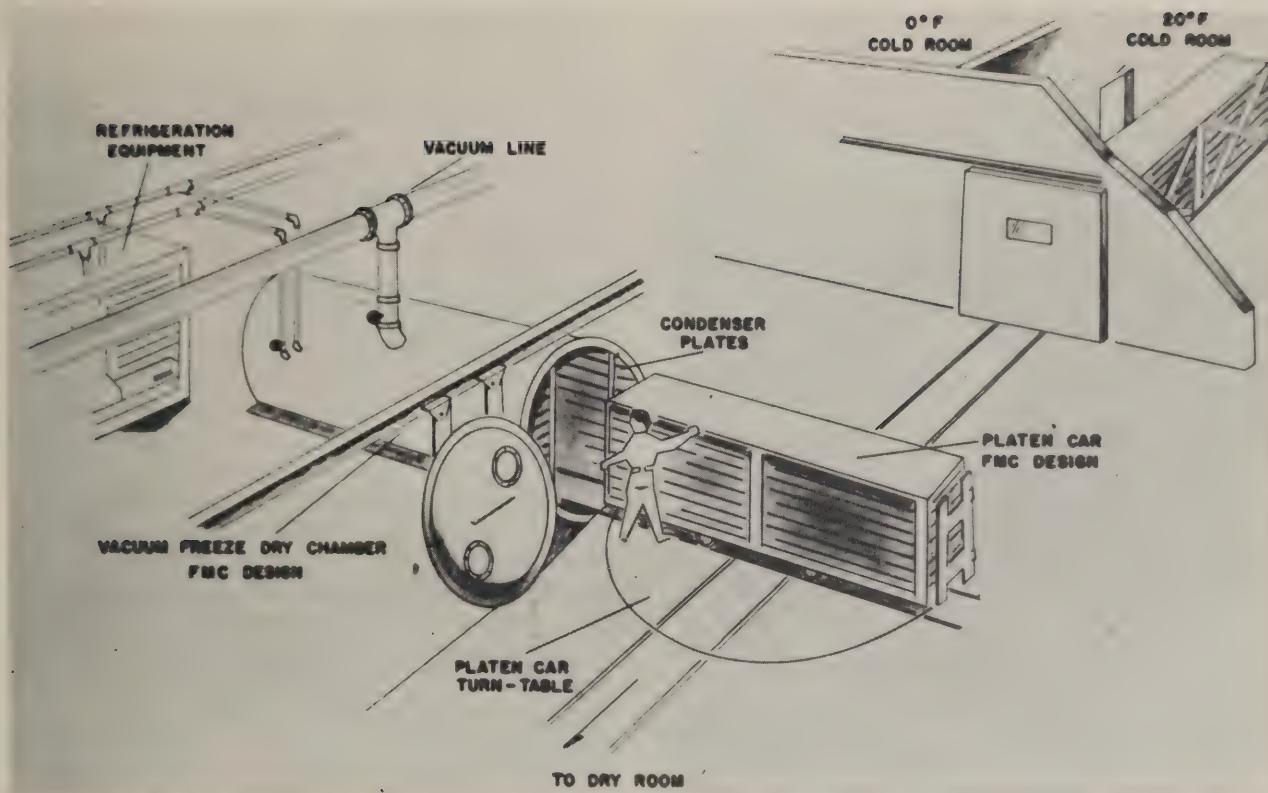


Figure 5. —Commercial freeze dehydration plant (schematic).

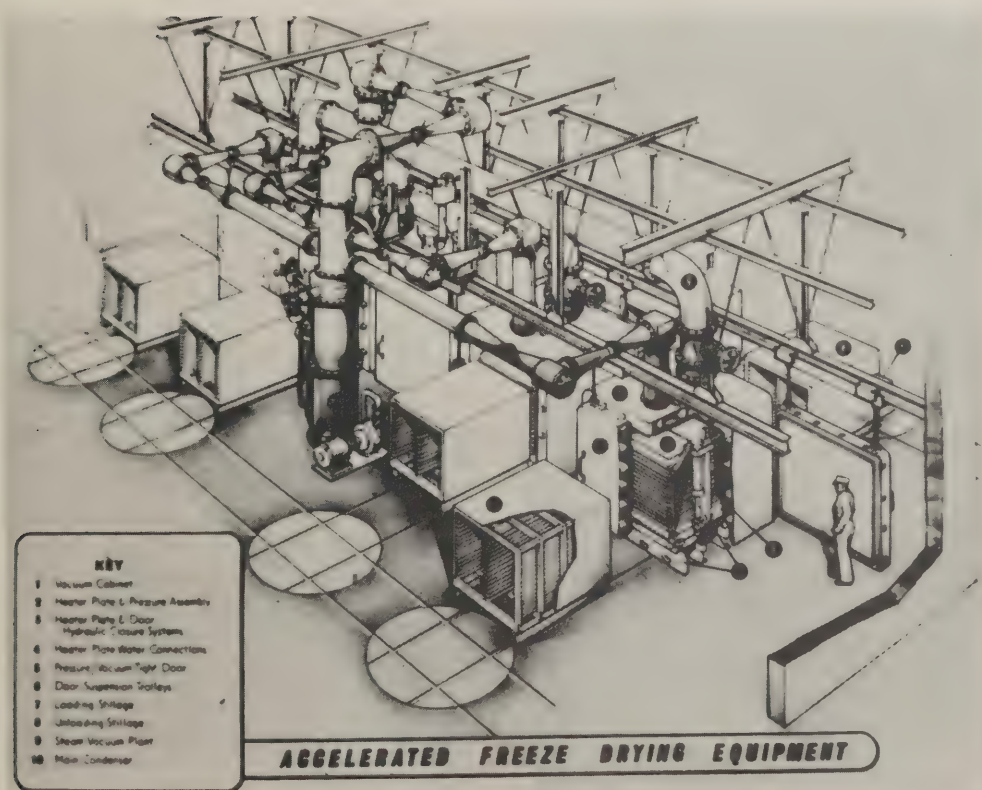


Figure 6. —Vickers accelerated freeze drying equipment.

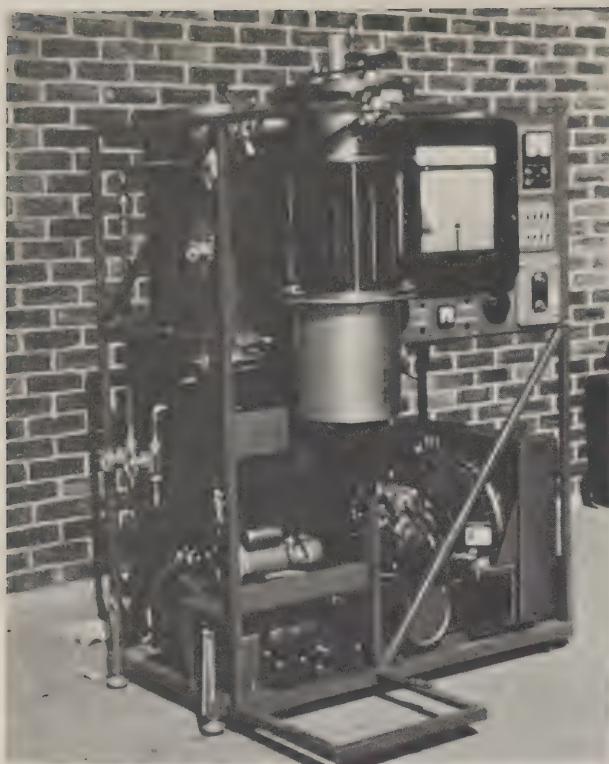


Figure 7.— Experimental tubular freeze drying unit. Liquid is frozen on exterior of tubes.

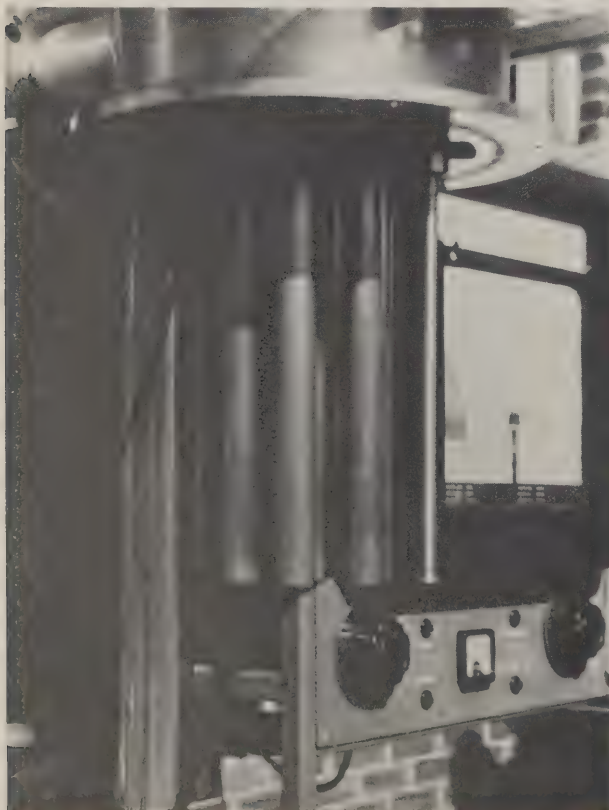


Figure 8.—Close-up of tube section (Figure 7).

on a portable trolley during a prefreeze period for the loaded trays and then wheeled into the drying chamber. Quick-coupling connections with a heating liquid system are employed. In other designs a portable tray carrier handles the trays thru the prefreeze operation in a blast cold room and is moved on a monorail or dolly into the chamber of the drying operation. This carrier so positions the trays that they are held equidistant from the heated shelves to achieve uniform heat transfer by radiation. Liquids such as coffee extract or citrus or tomato concentrate are generally frozen in a thin slab in trays, frequently inside of the chamber. Due to absence of adequate porosity in the frozen slab the rate of dehydration is extremely slow. Even periods as long as 48 hours may be needed for lyophilization. However, Prof. Louis Roy has demonstrated experimentally that if one freezes orange juice extremely quickly by means of liquid nitrogen and rewarms it to -60°C . prior to freeze-drying the period required can be cut in half. Another alternative is to freeze the liquid concentrate and then break it up mechanically into discrete small masses before spreading it on the trays. An objection to this is non-uniformity in drying because of the uneven distribution of heat to such irregular particles.

Overall, drying on trays inevitably extends the drying cycle quite materially. Heat transfer to a receding ice surface through the already dried outer layer of the frozen food product continually decreases in rate. This arises from the insulating effect of the dried shell, which is as effective as expanded polystyrene. This factor, added to initial high investment costs for the sophisticated freeze-drying equipment, raises drying costs far above those for other drying techniques.

During the past year two European firms have independently developed a new approach for lyophilization of liquids. They use nests of vertical stainless steel tubes inclosed in a shell similar in design to a vertical tubular condenser. Mitchell Engineering in their version freezes the liquid onto the exterior of the tubes, which for this purpose are flooded with a refrigerant on the inside. Based on a 6 mm. thick frozen layer of egg or fruit juice, which can be dried completely in $2\frac{1}{2}$ hours, cabinets have been designed to utilize a load of 560 lb. of raw

product per cycle, or about 2 tons per day. Figure 7 shows a view of an experimental unit, and Figure 8 a closeup view of the tubular section with the tubes raised away from the shell. No commercial plant has gone beyond the design stage but a pilot plant equipment of 19 tubes is now available for test purposes.

The commercial unit consists of a vertically mounted cylindrical shell 4 feet in diameter and 5 feet in height. A cluster of fingerlike tubes is suspended in the vertical plane and connected to a circulating fluid header tank mounted on top of the shell. The lower end of the cabinet is sealed with a removable end cover. With this removed the prechilled liquid product is lifted in a tank to bathe the tubes, on which a 6 mm. layer can be frozen in 5-6 minutes by circulating a refrigerating liquid at -25°F . Upon removal of this tank, the end cover is replaced and the system evacuated. Fluid at a temperature just below the eutectic point of the frozen liquid is circulated until sublimation is completed. Final drying is completed with the circulating liquid at no higher temperature than 90°F .

The refrigeration plant consists essentially of an H. P. compressor together with an L. P. compressor integrated into 3 main circuits, comprising one cooling and two heating circuits. The former passes through a low temperature brine cooler operating from the L. P. compressor. This circuit supplies cooling for the vapor condensers and also cools a cold brine reservoir during off-peak loads.

A subzero heating circuit, which supplies most of the heat needed for sublimation, passes through an intermediate brine-heater/cooler, which is itself operating from both the L. P. and H. P. compressors.

The secondary heating circuit passes through a brine heater operating on the high temperature side of the H. P. compressor. Mitchell has thus made effective use of the heat pump principle in the heating and refrigerating system with savings in energy of at least 30 percent.

Seffinga Engineering of Holland offers a similar design (figure 9) but one in which the liquid product is frozen on the inside of a bank

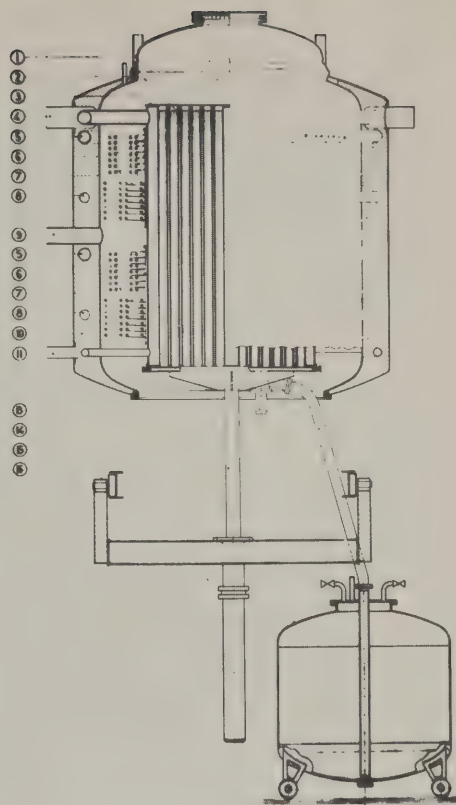


Figure 9.—Seffinga Engineering freeze drying unit for freezing liquids on interior of tubes.

of 162 vertical stainless steel tubes 1.75-2.0 inches in diameter and 6 feet high. The construction is similar to that of a shell and tube condenser, the tube bundle being completely enclosed by two tube plates and shell plates, making the space around the tubes an enclosed chamber which is connected to the NH_3 system. The tube bundle is placed in a vertical vessel of larger diameter, with removable s.s. end covers. The space between the two shells is the vacuum chamber, the condenser coils being located therein. During the freezing period the NH_3 is evaporated around the tubes. This cold liquid NH_3 is drained subsequently and warm NH_3 gas condensed on the tubes to supply heat needed to maintain sublimation of the ice in the frozen product. For filling, a tank of chilled liquid is connected through a pipe to the bottom of the tube bundle, a valve is opened pneumatically and nitrogen gas under pressure applied to force the liquid up into the tubes. The valve is then closed and refrigeration applied outside the tube walls. In about 10 minutes a layer 10 mm. thick has frozen onto the

DISCUSSION

inner surface of the tubes. By opening the valve at the bottom the excess unfrozen liquid flows back into the filling vessel. Vacuum is now applied inside the tubes and lyophilization proceeds. Deisel-driven Rolls-Royce compressors are employed. Material savings in fuel and electric power are realized. The operating cycle when drying a 10 mm. layer is about 8 hours, the vessel having a total charge of 1,300 lb. Daily throughput is 2.0 tons. Maximum temperature during drying is 100° F.

These tubular type freeze-driers seem a distinct advance for lyophilization of liquids. Heat transfer through the frozen ice layer in contact with the tube walls proceeds at a uniform rate until all ice is sublimed, instead of at a falling rate as is true in all tray driers. This speeds up the drying cycle considerably. A second advantage is that drying to low final moistures is attained without the product being exposed at anytime to temperature above body heat. Operation is highly automated. Throughput per dollar of capital investment is higher than in shelf dryers. Delivery of the dried product from the bottom of these vertical dryers can be automatically effected under an inert gas to the packaging room.

Two of the Seffinga dryers are being installed for drying liquid whole egg in the plant of Ranks, Hovis and McDougall at High Wycombe, England. I am assured that large-scale pilot plant studies have demonstrated that freeze dehydration of liquid egg in this equipment will cost no more than if it were spray dried, save for the difference in initial capital invested in the drying equipment. These dryers cost about \$80,000 each installed. Operating costs are calculated by Seffinga at \$13,000 per year of 250 days to dry 500 tons of liquid egg. This would work out to about 10¢/dry lb. However, with larger installations of higher capacity, they confidently expect to halve this figure.

While no large scale tests on citrus juices have been carried out in this new type of equipment they give every promise of affording a new method of commercial significance whereby superior dried products can be obtained at a cost which would make their marketing an attractive and profitable venture, provided adequate retail packaging at low cost can be developed.

Question: How do they remove that powder from inside of the tubes in the dryer?

J. H. Nair: Well, in the case of the Mitchell design scrapers are brought down from the top to scrape it off the outside surface of the tubes. In the case of the Seffinga design there is just enough shrinkage from the walls as the material dries so that it breaks free and quite clean. They place a screen close-up beneath the tubes so that this rounded shell of material can only fall a centimeter or two and support it there until the drying has been completed. Then they just let it fall down into the hopper where there is a screw conveyor that breaks it up and takes it away, all under nitrogen.

Question: When you use these tubes don't you have a tendency toward separation and segregation? When you use a dip and freeze and dip and freeze, and use it over again, you don't get a homogeneous product that would be well mixed at the end. Is that correct?

J. H. Nair: Now this I can't answer because not enough commercial experience has been obtained to know how serious a problem this may be. There is also a possibility that only half the liquid you have in this tank is used at one time and then you have to keep it refrigerated until you fill the next one. The concept is that with a series of dryers there would be such a short period of time between moving on to the next dryer that this time lapse would not be of great importance, but this visualizes, of course, large production. One of the major difficulties with freeze drying today anywhere in the world is that nobody has a really commercial sized operation. My experience indicates that if one is processing a natural product, 50 tons a day of raw material should be considered absolute minimum for a commercial throughput and 100 to 200 tons are needed if you are going to get real low cost operation. Nothing of this magnitude has yet come to the freeze drying industry, so we can't tell what the costs will be. I think the operation of Ranks, Hovis and McDougall will likely be the largest in the world when they get it going. They have invested 2 million dollars in equipment. They have this tubular dryer and they have shelf dryers which have been built by Seffinga.

Question: Is there enough improvement in quality in freeze dried orange juice to warrant costs like that?

J.H. Nair: I can't answer for orange juice because I haven't seen orange juice dried this way. I've eaten egg omelette made from egg powder dried this way which was the equal of a fresh egg omelette. You can dry whole eggs, which you cannot do with any

other process and get the same results, unless you add something to the egg like sucrose. It certainly recommends itself to me as an interesting development in freeze drying with a potential application to the citrus industry. With egg we start with 25 percent total solids and if we can start with 50 to 60 percent concentrate instead, we can cut our drying costs considerably and perhaps can get down to 5 cents per dry pound. I should think this would not be too bad a cost.

ATTENDANCE LIST

Albach, Dr. Roger F., Fruit and Veg.
Prod. Lab., Weslaco, Tex. 78596

Ambrose, Donald, Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33882

Atkins, C.D., Florida Citrus Comm., Lake
Alfred, Fla. 33850

Attaway, Dr. John, Florida Citrus Comm.,
Lake Alfred, Fla. 33850

Barkley, John N., FMC Corp., P.O. Box
1708, Lakeland, Fla. 33850

Barron, R.W., Florida Citrus Comm.,
Lake Alfred, Fla. 33850

Beavens, Dr. E.A., Chief, Fruit and Veg.
Chem. Lab., Pasadena, Calif. 91106

Berry, Dr. R.E., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33882

Bissett, Owen W., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33882

Bitzick, George M., Interntl. Flavors &
Fragrances, Inc., 521 W. 57th St.,
N. Y., N. Y. 10019

Blagg, Al., Winter Garden Citrus Prod.
Coop., P.O. Box 399, Winter Garden,
Fla. 32787

Blair, Dr. J.S., Stetson Univ., P.O. Box
314, DeLand, Fla. 32721

Bonnell, Dr. J.M., Tropicana Prod., Inc.,
Bradenton, Fla. 33506

Boyd, J.M., Continental Can Co., 1350 W.
76th St., Chicago, Ill. 60620

Brent, Dr. J.A., Coca-Cola Co., 310 North
Ave. N.W., Atlanta, Ga. 30313

Bradner, Saidee E., HiAcres Concentrate,
Inc., Box 7127, Orlando, Fla. 32804

Brown, J.W., Pasco Packing Co., Dade
City, Fla. 33525

Brown, W.W., Pasco Packing Co., Dade
City, Fla. 33525

Bucek, Wesley A., Minute Maid Co.,
Plymouth, Fla. 32768

Carter, R.D., Cypress Gardens Citrus
Prods. Inc., P.O. Box 1312, Winter
Haven, Fla. 33881

Chartor, L.C., Durkee Famous Foods,
419 Sevilla Ave., Coral Gables, Fla.
33134

Clark, C.W., Minute Maid Co., 1200 W.
Colonial Dr., Orlando, Fla. 32802

Clevenger, H.L., FMC Corp., P.O. Box
1708, Lakeland, Fla. 33802

Cooper, Dr. W.C., USDA Hort. Field Sta.,
2120 Camden Road, Orlando, Fla. 32803

Cox, W. Martin, Cadbury Bros. Ltd.,
Bournville, Birmingham, England

Cranfield, Dale, Minute Maid Co.,
Plymouth, Fla. 32768

Davis, Paul, USDA, AMS, 2120 Camden
Road, Orlando, Fla. 32803

Dennison, Dr. R.A., Univ. of Fla., Food
Tech. Dept., Gainesville, Fla. 32603

- Doll, Frederick E., Continental Can Co.,
1536 Valencia St., Clearwater, Fla.
33516
- DuBois, C.W., Minute Maid Co., Ply-
mouth, Fla. 32768
- Duffy, Charles J., Mission Orange De
Mexico, SA, Apartado Postal 1973,
Mexico City, Mexico 1, D. F.
- Edwards, George J., Citrus Expt. Sta.,
Lake Alfred, Fla. 33850
- Enns, W.G., Continental Can Co., Lake
Howard Dr., Winter Haven, Fla. 33880
- Estes, D.L., Libby, McNeill & Libby,
Ocala, Fla. 32670
- Fellers, Dr. Paul J., Florida Citrus
Comm., Lake Alfred, Fla. 33850
- Fisher, Dr. James F., Fruit & Veg. Prod.
Lab., Winter Haven, Fla. 33882
- Fox, C.J., Hercules Powder Co., 1203
Wachovia Bank Bldg., Charlotte, N.C.
28202
- Gerwe, Dr. Ray D., FMC Corp., Lakeland,
Fla. 33802
- Gray, L.E., FMC Corp., Lakeland, Fla.
33802
- Greene, Tom, Tropicana Prod., Inc.,
Bradenton, Fla. 33506
- Grinnell, Philip C., Minute Maid Co., Ply-
mouth, Fla. 32768
- Griffiths, Dr. F.P., Fruit and Veg. Prod.
Lab., Weslaco, Tex. 78596
- Hamrick, David, Tropicana Prod., Inc.,
Bradenton, Fla. 33506
- Hanley, Joseph W., Libby, McNeill & Libby,
1800 W. 119th St., Chicago, Ill. 60643
- Hannan, Harry Jr., Crown Cork & Seal Co.,
P.O. Box 513, Orlando, Fla. 32802
- Frosher, James L., Fruit & Veg. Prod.
Lab., Winter Haven, Fla. 33882
- Harris, Donald F., Birds Eye Div. of Gen-
eral Foods, Drawer B, Florence Villa Sta.,
Winter Haven, Fla. 33882
- Hartman, Gordon D., Tropicana Prod., Inc.,
P.O. Box 338, Bradenton, Fla. 33506
- Hastings, Kenneth W., Lake Hamilton Con-
centrates, Inc., Bartow, Fla. 33830
- Hendrickson, R., Citrus Expt. Sta., Lake
Alfred, Fla. 33850
- Hendrix, Charles Jr., Redd Labs., Inc.,
507 S. Seminole Rd., Largo, Fla. 33540
- Hester, O.C., Econ. Res. Div., South.
Util. Res. & Dev. Div., P.O. Box 19687,
New Orleans, La. 70119
- Hill, E.C., Florida Citrus Comm., Citrus
Expt. Sta., Lake Alfred, Fla. 33850
- Hope, Landon, B & W Canning Co., Grove-
land, Fla. 32736
- Huber, Dorothy Ann, Continental Can Co.,
Metals R & D., 1350 W. 76th St., Chicago,
Ill. 60620
- Huggart, R.L., Florida Citrus Comm.,
Citrus Expt. Sta., Lake Alfred, Fla. 33850
- Hull, James S., Container Corp. of America,
Fibre Can Div., Rt. 1, Box 288, Orlando,
Fla. 32802
- Hunter, Dr. G.L.K., Minute Maid Co., 1200
Colonial Dr., Orlando, Fla. 32802
- Inglett, G.E., Int'l. Minerals & Chem.
Corp., Skokie, Ill. 60078
- Jefferson, Jon E., Redd Labs., 1711 S. 10th
St., Safety Harbor, Fla. 33572
- Kew, Theo. J., Fruit & Veg. Prod. Lab.,
Winter Haven, Fla. 33882
- Kilburn, R.W., Florida Citrus Canners
Coop., Drawer 111, Lake Wales, Fla.
33853
- Kortschot, Cornelis, Plant Inds., Inc.,
Orange Crystals Div., P. O. Box 1550,
Plant City, Fla. 33566
- Lastinger, Jack, Fruit and Veg. Prod. Lab.,
Winter Haven, Fla. 33882
- Lund, A. F., Miller-Lenfestey Supply
Co., P. O. Box 3384, Tampa, Fla.
33601

- McAllister, J.W., USDA, Processed Foods Inspection, P.O. Box 860, Winter Haven, Fla. 33881
- MacDowell, Dr. L.G., Florida Citrus Comm., P.O. Box 148, Lakeland, Fla. 33802
- McDuff, O.R., Adams Packing Assoc., P.O. Box 37, Auburndale, Fla. 33823
- McFarlane, Dr. V.H., FC Lab., South. Util. Res. & Dev. Div., P.O. Box 19687, New Orleans, La. 70119
- McKinnis, Dr. R.B., Brown Citrus Machinery Corp., 333 Ave. M - N.W., Winter Haven, Fla. 33880
- Matthews, Richard F., Dept. of Food Technol., Univ. of Fla., Tallahassee, Fla. 32306
- Meunier, Vincent, Rohm & Haas, Lawton Road, Charlotte, N.C. 28214
- Miller, Bruce D., Votator Div., Chemetron Corp., Winter Park, Fla. 32790
- Miller, W.H., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33882
- Moore, Dr. E.L., Florida Citrus Comm., Citrus Expt. Sta., Lake Alfred, Fla. 33850
- Moshonas, M.G., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33850
- Muncie, Dr. F.W., Suni-Citrus Prod., Haines City, Fla. 33844
- Murdock, D.I., Minute Maid Corp., Plymouth, Fla. 32768
- Naguib, Shahier, Winter Garden Citrus Prod. Corp., Winter Garden, Fla. 32787
- Nair, Dr. J.H., Research Consultant, Pres-Elect IFT, 2424 Wentworth St., Raleigh, N.C. 27609
- Neubert, A.M., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33882
- Newhall, Dr. William F., Citrus Expt. Sta., Lake Alfred, Fla. 33850
- Nordby, Dr. Harold E., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33882
- Olsen, Robert W., Citrus Expt. Sta., Lake Alfred, Fla. 33850
- Parish, Elmer C., Crown Cork & Seal Co., 2806 Lion Heart Road, Winter Park, Fla. 32790
- Pinner, Ann S., USDA, AMS, Proc. Foods, P. O. Box 860, Winter Haven, Fla. 33881
- Pisano, Charles, Citrus & Allied Essential Oils Co., 65 So. Tyson Ave., Florham Park, N. J. 07932
- Porcara, Peter, Givaudan Corp., Delawanna Ave., Clifton, N.J. 07014
- Potter, R., Givaudan Flavors, 321 West 44th St., New York, N. Y. 10036
- Powers, A. J., Juice Corp. of America, Inc., Highlands City, Fla. 33846
- Praschan, V. C., Fruit & Veg. Prod. Lab., National Dairy Prods. Corp., 801 Waukegan Road, Glenview, Ill. 60025
- Pulley, G.N., Cypress Gardens Citrus Prod., Inc., Winter Haven, Fla. 33881
- Rafter, Ann Marie, Minute Maid Co., Res. & Dev. Dept., Plymouth, Fla. 32768
- Ratcliff, Morris W., Fla. Citrus Cannery Coop., Lake Wales, Fla. 33853
- Reingold, George, Continental Can Co., 315 Madison St., Tampa, Fla. 33602
- Reitz, Dr. Herman J., Citrus Expt. Sta., Lake Alfred, Fla. 33850
- Roberson, John P., Chas. Pfizer & Co., Inc., 1370 Valley View Rd., Danwood, Ga. 30043
- Rogers, J.A., Fritzsche Bros., Inc., 76 9th Ave., New York, N. Y. 10011
- Rogers, Robert O., Prod. & Proc. Eval. Staff, USDA, ARS, Washington, D.C. 20250
- Rouse, A.H., Citrus Expt. Sta., Lake Alfred, Fla. 33850

- Schaible, C.H., Florida Grower & Rancher, P. O. Box 52, Winter Haven, Fla. 33881
- Schlegel, W., Givaudan-Esrolko Ag., 8600 DuBendorf, Switzerland
- Schulz, H. E. (Bert), Florida Chem. Co., Box 997, Lake Alfred, Fla. 33850
- Scott, W. Clifford, Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33850
- Seiler, Robert R., Minute Maid Co., Plymouth, Fla. 32768
- Senti, F. R., Deputy Administrator, NCIUR, ARS, USDA, Washington, D. C. 20250
- Shaw, Dr. Philip E., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33850
- Shearin, Earl, Salada-Sherriff-Horsey, Inc., Plant City, Fla. 33566
- Smith, C. B., Quality Control Dept., Plymouth Citrus Prod. Coop., Plymouth, Fla. 32768
- Stanley, W. L., Fruit Lab., West. Util. Res. & Dev. Div., 800 Buchanan, Albany, Calif. 94710
- Stowe, W. M., Suni-Citrus Prod., Haines City, Fla. 33844
- Sutherland, C. Reed, Birds Eye Div. of Gen. Foods, Florence Villa Station, Winter Haven, Fla. 33882
- Swift, Dr. Lyle J., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33882
- Tatum, James H., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33882
- Ting, Dr. S. V., Florida Citrus Comm., Lake Alfred, Fla. 33850
- Traviss, James J., Holly Hill Fruit Products Co., Davenport, Fla. 33837
- Trumm, Howard W., Libby, McNeill & Libby, Ocala, Fla. 32670
- Veldhuis, Dr. M.K., Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33882
- Viale, Hector, Adams Packing Assoc., Auburndale, Fla. 33823
- Wagner, Charles J. Jr., Fruit and Veg. Prod. Lab., Winter Haven, Fla. (FCC) 33882
- Watkins, Wayne J., Tropicana Prod., Inc., Bradenton, Fla. 33506
- Wenzel, Dr. F.W., Citrus Expt. Sta., Lake Alfred, Fla. 33850
- Westbrook, Dr. Geo. F., Fla. Dept. of Agric., Winter Haven, Fla. 33880
- Willard, Robert P., Adams Packing Assoc., Auburndale, Fla. 33823
- Wilson, Charles W. III, Fruit and Veg. Prod. Lab., Winter Haven, Fla. 33882
- Wojcik, Dr. B. H., South. Util. Res. & Dev. Div., P. O. Box 19687, New Orleans, La. 70119
- Wolford, Richard W., Florida Citrus Comm., c/o Citrus Expt. Sta., Lake Alfred, Fla. 33850
- Worden, Stan., Tropicana Prod., Inc., Bradenton, Fla. 33506
- Young, David, Miller-Lenfestey Supply Co., P.O. Box 3384, Tampa, Fla. 33601
- Young, W. H., Plymouth Citrus Prod. Coop., Plymouth, Fla. 32768

UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Service

**LIST OF
CITRUS PUBLICATIONS
AND PATENTS**

(September 1, 1963 - August 31, 1965)

Reprints of publications may be obtained without cost by
addressing request to the Laboratory listed.

Patents may be obtained only by purchase from the U. S. Patent
Office, Washington, D. C. 20250, for 50 cents each.

SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

FRUIT AND VEGETABLE PRODUCTS LABORATORY

600 Avenue S, N.W.
Winter Haven, Florida 33882

FLOAT CHECK VALUE FOR USE WITH A WATER ASPIRATOR

Swift, Lyle James
Chemist Analyst 52, 23 (1963)

IDENTIFICATION AND DETERMINATION OF AN ADULTERANT IN CITRUS OILS

Hunter, G. L. K.
J. Assoc. Office. Agr. Chemists 46,
838-840 (1963)

CHANGES IN TOTAL CARBONYL CONTENT OF ORANGE JUICE AND CONCENTRATE DURING STORAGE

Senn, Vincent J.
J. Food Sci. 28, 531-536 (1963)

ISOLATION OF BETA-ELEMENE FROM ORANGE OIL

Hunter, G. L. K. and Parks, G. L.
J. Food Sci. 29, 25-26 (1964)

2,4-p-MENTHADIENE. A NEW MONOTER- PENE FROM VALENCIA ORANGE OIL

Hunter, G. L. K. and Brogden, W. B., Jr.
J. Org. Chem. 29, 498-499 (1964)

THE REARRANGEMENT OF LIMONENE AND CARVOMENTHENE EPOXIDES

Settine, R. L., Parks, G. L., and
Hunter, G. L. K.
J. Org. Chem. 29, 616-618 (1964)

STRUCTURE OF YLANGENE

Hunter, G. L. K. and Brogden, W. B., Jr.
J. Org. Chem. 29, 982-983 (1964)

THE EFFECT OF BENZOIC, SORBIC, AND DEHYDROACETIC ACIDS ON THE GROWTH OF CITRUS PRODUCTS SPOILAGE ORGAN- ISMS

Rushing, N. B. and Senn, Vincent J.
Proc. Florida State Hort. Soc. 76,
271-276 (1963)

GENERAL APPLICATION OF NEAR-INFRA- RED MOISTURE ANALYSIS TO FRUIT AND VEGETABLE MATERIALS

Gold, Harvey J.
Food Technol. 18, 184-185 (1964)

A RAPID METHOD FOR ISOLATION AND IDENTIFICATION OF SESQUITERPENE HYDROCARBONS IN COLD-PRESSED GRAPEFRUIT OIL

Hunter, G. L. K. and Brogden, W. B., Jr.
Anal. Chem. 36, 1122-1123 (1964)

B-YLANGENE, A NEW SESQUITERPENE HYDROCARBON FROM ORANGE OIL

Hunter, G. L. K. and Brogden, W. B., Jr.
J. Org. Chem. 29, 2100 (1964)

SHELF LIFE OF CHILLED ORANGE JUICE WITH HEAT TREATMENT AND PRESERVA- TIVES

Rushing, N. B. and Senn, Vincent, Jr.
Food Technol. 18, 112-114 (1964)

PROCEEDINGS OF THE CITRUS PROCESS- ING CONFERENCE (1963)

Compiled by B. A. Sharar
U. S. Dept. Agr. ARS 72-28, 30 pages
(1964)

MODIFIED INFRARED SALT PLATE FOR LIQUID MICROLITER SAMPLES WITHOUT BEAM CONDENSER

Hunter, G. L. K.
Appl. Spectry. 18, 159 (1964)

ISOLATION OF 5,6,7,3',4'-PENTAMETH- OXYFLAVONE FROM ORANGE-PEEL JUICE

Swift, Lyle J.
J. Food Sci. 29, 766-767 (1964)

MASS SPECTROMETRIC SAMPLING FROM MICRO INFRARED PLATES AND RECOL- LECTION OF SAMPLE FOR FURTHER ANALYSIS

Moshonas, M. G. and Hunter G. L. K.
Appl. Spectry. 18, 193 (1964)

COMPARISON OF ORANGE CONCENTRATE AND FOAM-MAT POWDERS USING CHROM- ATOGRAPHIC PROCEDURES

Tatum, J. H., Parks, G. L., and Berry, R. E.
The Citrus Industry 46, No. 2, 8, 10,
11, 26 (1965)
Proc. Florida State Hort. Soc. 77,
307-311 (1964, pub. 1965)

ISOLATION AND IDENTIFICATION OF
ALCOHOLS IN COLD-PRESSED VALENCIA
ORANGE OIL BY LIQUID-LIQUID EXTRAC-
TION AND GAS CHROMATOGRAPHY

Hunter, G. L. K. and Moshonas, M. G.
Anal. Chem. 37, 378-380 (1965)

TERPENES AND SESQUITERPENES IN
COLD-PRESSED ORANGE OIL

Hunter, G. L. K. and Brogden, W. B., Jr.
J. Food Sci. 30, 1-4 (1965)

EFFECT OF VITAMIN K₅ ON ASCORBIC
ACID STABILITY IN ORANGE JUICE

Rushing, N. B. and Senn, V. J.
J. Food Sci. 30, 178-180 (1965)

FOAM-MAT-DRIED GRAPEFRUIT JUICE.
TIME-TEMPERATURE DRYING STUDIES

Berry, R. E., Bissett, O. W.,
Wagner, C. J., Jr., and Veldhuis, M. K.
Food Technol. 19, 426-428 (1965)

PROXIMATE ANALYSES OF FLORIDA
ORANGE PEEL JUICE EXTRACT FOR THE
1962-63 AND 1963-64 SEASONS

Swift, Lyle J.
J. Agr. Food Chem. 13, 282-284 (1965)

ANALYSIS OF THE TERPENE AND SES-
QUITERPENE HYDROCARBONS IN SOME
CITRUS OILS

Hunter, G. L. K. and Brogden,
W. B., Jr.
J. Food Sci. 30, 383-387 (1965)

TETRA-O-METHYLSCUTELLAREIN IN
ORANGE PEEL

Swift, Lyle J.
J. Org. Chem. 30, 2079-2080 (1965)

BULK DENSITY AND RECONSTITUTION
RATES OF FOAM-MAT DRIED CITRUS
POWDERS

Wagner, C. J., Jr., Bissett, O. W.,
and Berry, R. E.
Proc. Florida State Hort. Soc. 77,
311-315 (1964, pub. 1965)

METHOD FOR EVALUATING FOAMS
FROM CITRUS CONCENTRATES

Berry, R. E., Bissett, O. W., and
Lastinger, J. C.
Food Tech. 19, 144-147 (1965)

U. S. FRUIT AND VEGETABLE PRODUCTS LABORATORY

P. O. Box 388
Weslaco, Texas 78596

BIOSYNTHETIC RELATIONSHIPS BE-
TWEEN CAROTENENES

Purcell, A. E.
Arch. Biochem. Biophys. 105, 606-
611 (1964)

INFLUENCE OF FRUIT AGE ON LYCOPENE
CONCENTRATION IN COLORED GRAPEFRUIT

Purcell, A. E. and Schultz, E. F., Jr.
Proc. Am. Soc. Hort. Sci. 85, 183-
188 (1964)

WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

WESTERN REGIONAL RESEARCH LABORATORY

800 Buchanan Street
Albany, California 94710

VOLATILES FROM ORANGES. I. HYDRO-
CARBONS IDENTIFIED BY INFRARED
NUCLEAR MAGNETIC RESONANCE AND
MASS SPECTRA

Teranishi, Roy, Schultz, Thomas H.,
McFadden, W. H., Lundin, R. E., and
Black, D. R.
J. Food Sci. 28, 541-545 (1963)

LABORATORY COLLOID MILL FOR PRE-
PARATION OF LOCKED-IN FRUIT
FLAVORS WITH AMORPHOUS SUGARS

Schultz, T. H. and Rockwell, W. C.
Food Technol. 17, 100-102 (1963)

NMR STUDY OF TRIMETHYLSILYL ETHERS
OF FLAVONOID COMPOUNDS

Waiss, A. C., Jr., Lundin, R. E., and
Stern, D. J.
Tetrahedron Letters 10, 513-518 (1964)

RECENT DEVELOPMENTS IN COUMARIN
CHEMISTRY

Stanley, William L.
In "Aspects of Plant Phenolic Chemis-
try," Proc., 3rd Ann. Symp. Plant
Phenolics Group of North America,
Toronto, Sept. 6-7, 1963, pp. 79-103,
(1964)

FOAMS FOR FOAM-MAT DRYING

Hart, M. R., Graham, R. P.,
Ginnette, L. F., and Morgan, A. I., Jr.
Food Technol. 17, 90-92 (1963)

WHAT CAN BE DONE IN FLAVOR RE- SEARCH

Stanley, William L.
Calif. Olive Assoc. Ann. Tech. Rept.
1963, 67-76 (1964)

DEHYDROXYLATION OF CAFFEIC ACID BY RAT AND RABBIT CAECAL CONTENTS AND SHEEP RUMEN LIQUOR

Booth, A. N., Williams, R. T. (St.
Mary's Hospital Medical School, Padding-
ton, London W2)
Nature 198, 684-685 (1963)

DEHYDROXYLATION OF CATECHOL ACIDS BY INTESTINAL CONTENTS

Booth, A. N. and Williams, R. T. (St.
Mary's Hospital Medical School,
Paddington, London W2)
Proc., Biochem. Soc. 429th, June 27-
28, 1963, bound with Biochem. J. 88,
66P-67P (1963)

SELECTIVE PARA- OR META-O-METHYL- ATION WITH CATECHOL O-METHYL TRANSFERASE FROM RAT LIVER

Masri, M. S., Robbins, D. J., Emerson,
O. H., and DeEds, F.
Nature 202, 878-879 (1964)

METHYLATION OF POLYHYDROXY-ARO- MATIC COMPOUNDS BY PAMPAS GRASS O-METHYLTRANSFERASE

Finkle, B. J. and Masri, M. S.
Biochem. et Biophys. Acta 85, 167-
169 (1964)

VACUUM-SPRAY EVAPORATOR

Schultz, W. G.
Food Eng. 36, 62-63 (1964)

VOLATILES FROM ORANGES. II. CON- STITUENTS OF THE JUICE IDENTIFIED BY MASS SPECTRA

Schultz, T. H., Teranishi, Roy,
McFadden, W. H., Kilpatrick, P. W.,
and Corse, Joseph
J. Food Sci. 29, 790-795 (1964)

AURAPTENOL, A COUMARIN COMPOUND IN BITTER (SEVILLE) ORANGE OIL

Stanley, W. L., Waiss, A. C., Jr.,
Lundin, R. E., and Vannier, S. H.
Tetrahedron 21, 89-92 (1965)

ALLERGY TO GREEN COFFEE. FAILURE
OF PATIENTS ALLERGIC TO GREEN
COFFEE TO REACT TO CHLOROGENIC
ACID, ROASTED COFFEE, OR ORANGE
Layton, L. L., Greene, F. C., Panzani,
Raphael, with assistance of Corse, J. W.
J. Allergy 36(1), 84-91 (1965)

THE OCCURRENCE OF BETA-CITRAURIN AND OF BETA-APO-8'-CAROTENAL IN THE PEELS OF CALIFORNIA TANGERINE AND ORANGES

Curl, A. L.
J. Food Sci. 30, 13-18 (1965)

PHOTOOXIDATIVE CYCLIZATION OF QUERCETIN PENTAMETHYL ETHER

Waiss, A. C., Jr. and Corse, Joseph
J. Am. Chem. Soc. 87, 2068-2069
(1965)

VOLATILES FROM ORANGES. III. THE STRUCTURE OF SINENSAL

Stevens, K. L., Lundin, R. E., and
Teranishi, R.
J. Org. Chem. 30, 1690-1692 (1965)

IDENTIFICATION OF SEVERAL COMPO- NENTS OF ISOCHLOROGENIC ACID

Corse, Joseph, Lundin, R. E., and
Waiss, A. C., Jr.
Phytochem. 4, 527-529 (1965)

STRUCTURE OF THE CAROTENOID NEOX- ANTHIN

Curl, A. L.
J. Food Sci. 30, 426-432 (1965)

PATENTS

(All patents are assigned to U. S. Govern-
ment as represented by the Secretary of
Agriculture)

EXTRACTION OF FLAVORS

W. L. Stanley, J. E. Brekke, and Roy
Teranishi
U. S. Patent No. 3,113,031, Dec. 3,
1963

PREPARATION OF FLAVOR COMPOSI- TIONS

Schultz, T. H. and Rockwell, W. C.
Patent No. 3,183,099, May 11,
1965

FRUIT AND VEGETABLE CHEMISTRY LABORATORY
263 South Chester Avenue
Pasadena, California 91106

COMPOSITION OF CITRUS OILS. ISOLA-
TION, IDENTIFICATION, AND GAS CHRO-
MATOGRAPHIC ESTIMATION OF SOME
ESTERS AND ALCOHOLS OF LEMON OIL

Ikeda, R. M. and Spitler, E. M.

J. Agr. Food Chem. 12, 114-117
(1964)

[CITRUS BITTER PRINCIPLES. I.] A
BIOGENETIC PROPOSAL FOR THE SEMI-
ROUBACEOUS BITTER PRINCIPLES

Dreyer, David L.

Experientia 20(6), 297-298 (1964)

RELATIONS BETWEEN THE TASTE AND
STRUCTURE OF SOME PHENOLIC GLYCO-
SIDES

Horowitz, Robert M.

Chap. 14 in "Biochemistry of Phenolic
Compounds," ed. by J. B. Harborne,
Academic Press, London and New
York, pp. 546-571 (1964)

STRUCTURE OF VITEXIN AND ISOVI-
TEXIN

Horowitz, R. M. and Gentili, Bruno

Chem. & Indus. 12, 498-499 (1964)

NUCLEAR HYDROGEN-DEUTERIUM EX-
CHANGE IN RESORCINOLS AND RELATED
COMPOUNDS IN WEAKLY ALKALINE
SOLUTION

Hand, Eli S. and Horowitz, R. M.

J. Am. Chem. Soc. 86, 2084-2085
(1964)

SESQUITERPENES. I. NOOTKATONE, A
NEW GRAPEFRUIT FLAVOR CONSTITUENT

MacLeod, W. D., Jr. and Buigues, N.M.

J. Food Sci. 29, 565-568 (1964)

FLAVONOIDS OF CITRUS. VII. LIMO-
CITROL AND ISOLIMOCITROL

Gentili, Bruno and Horowitz, R. M.

Tetrahedron 20, 2313-2316 (1964)

THE DETECTION OF BENZYL ETHER
ADDED TO LEMON OIL

MacLeod, W. D., Jr., Lundin, R. E.,
and Buigues, Nelida M.

J. Food Sci. 29, 802-803 (1964)

FLAVONOIDS OF CITRUS. VIII. SYN-
THESIS OF LIMOCITROL, LIMOCITRIN
AND SPINACETIN

Dreyer, D. L., Tabata, S., and Horowitz,
R. M.

Tetrahedron 20, 2977-2983 (1964)

CITRUS BITTER PRINCIPLES. II. APPLI-
CATION OF NMR TO STRUCTURAL AND
STEREOCHEMICAL PROBLEMS

Dreyer, D. L.

Tetrahedron 21, 75-87 (1965)

CITRUS BITTER PRINCIPLES. III. ISO-
LATION OF DEACETYLNOMILIN AND
DEOXYLIMONIN

Dreyer, D. L.

J. Org. Chem. 30, 749-751 (1965)

COLLABORATIVE STUDIES ON CHARACT-
ERIZATION OF LEMON JUICE

Yokoyama, Henry

J. Assoc. Office Agr. Chemists 48,
530-533 (1965)

CITRUS CAROTENOIDS. II. THE
STRUCTURE OF CITRANAXANTHIN, A
NEW CAROTENOID KETONE

Yokoyama, Henry and White, M. J.

J. Org. Chem. 30, 2481-2482
(1965)

CITRUS CAROTENOIDS. III. THE
STRUCTURE OF RETICULATAXANTHIN

Yokoyama, Henry, White, M. J., and
Vandercook, C. E.

J. Org. Chem. 30, 2482-2483 (1965)

**UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE**

SOUTHERN UTILIZATION RESEARCH & DEVELOPMENT DIVISION

P. O. BOX 19687

NEW ORLEANS, LOUISIANA 70119

OFFICIAL BUSINESS

**POSTAGE AND FEES PAID
U. S. DEPARTMENT OF AGRICULTURE**

A3288